

The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

Effects of the Uronic Acid Carboxyls on the
Sorption of 4-O-Methylglucuronoarabinoxylans
and Their Influence on Papermaking
Properties of Cellulose Fibers

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June, 1964

EFFECTS OF THE URONIC ACID CARBOXYLS ON THE SORPTION OF
4-O-METHYLGLUCURONARABINOXYLANS AND THEIR INFLUENCE
ON PAPERMAKING PROPERTIES OF CELLULOSE FIBERS

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in partial fulfillment of the requirements
of The Institute of Paper Chemistry
for the degree of Doctor of Philosophy
from Lawrence College,
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June, 1964

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SUMMARY

An experimental program was performed to test the hypothesis that the uronic acid carboxyls affect sorption of hemicelluloses and influence the paper-making properties of cellulose fibers. The experimental program consisted of preparation and examination of two pulps on which hemicelluloses with different carboxyl contents were sorbed. One pulp was prepared by sorption of a hemicellulose containing uronic acid carboxyls and the second pulp was prepared by sorption of an equal quantity of the same hemicellulose after partial reduction of the uronic acid carboxyls.

The hemicellulose polymer, 4-O-methylglucuronoarabinoxylan (GAX), was isolated by alkaline extraction from an alkaline sulfite (sulfide) spruce pulp. A portion of this polymer (fully acetylated) was subjected to gaseous diborane reduction resulting in reduction of 60% of the uronic acid carboxyls to primary alcohol groups in this portion. Fractionation and determination of the weight to number average molecular weight ratio of the fully acetylated unreduced polymer indicated that this polymer had a fairly narrow molecular weight distribution. It was shown that the reduction procedure caused little change in the molecular weight of the polymer.

Partial reduction of the uronic acid carboxyls lowered the solubility of the reduced polymer in water. This reduction in solubility increased significantly the sorption of the reduced polymer upon a beaten, classified cotton linters pulp in water. The solubility of the hemicellulose due to the carboxyls was suppressed when 0.02N hydrochloric acid was used as the solvent and comparable retentions of the reduced and unreduced polymers were achieved. The retention of the reduced polymer from 0.02N hydrochloric acid was more than two orders of magnitude greater than that observed when water was used as the sorption

solvent, whereas the unreduced polymer retention was nearly four times greater from 0.02N hydrochloric acid under comparable conditions. There was no indication of preferential sorption of polymer species of higher or lower carboxyl content in the presence of hydrochloric acid.

Intrinsic viscosities of the polymers remaining in the supernatant solution after sorption were much lower than those of the original polymers indicating that preferential sorption of higher molecular weight species occurred on a cellulose substrate with the material and conditions used in this study. The sorption conditions had little or no effect on the intrinsic viscosity of either polymer in the absence of pulp.

Sorption of these reduced and unreduced polymers on beaten, classified cotton linters produced two pulps which appear essentially identical in composition except for their uronic acid carboxyl contents. A comparison of these two pulps and the untreated control pulp showed that the presence of the sorbed hemicellulose and its uronic acid salts apparently increased the amount of accessible fibrillar area. This increase in accessible fibrillar area was realized by an increase in the filtration resistance of the pulps containing sorbed hemicellulose with the uronic acid carboxyls in the salt form, whereas much lower values were observed with these carboxyls in the acid form. Filtration resistance increased more rapidly with beating, and handsheet strength properties were improved when these uronic acid salts were present. The compressibility of the cellulose substrate was increased by the presence of the sorbed hemicellulose probably due to a "lubrication effect" which increased interfiber slippage.

INTRODUCTION

Although there is general agreement that the presence of hemicelluloses contributes significantly to pulp properties, there is only limited knowledge concerning the effects of specific chemical and physical configurations of hemicelluloses upon pulp properties. Workers in this area have experienced considerable difficulty in designing experimental techniques to isolate and study particular polymer characteristics because hemicelluloses are heterogeneous not only in molecular weight and molecular weight distribution, but also in chemical composition and structure. Studies on the role of hemicelluloses in the papermaking properties of pulps will be reviewed briefly here. Detailed reviews of the literature have been published by Wise (1), Swanson (2), McKenzie and Higgins (3), and Dickey (4).

Studies on the effects of hemicelluloses on pulp properties have been based on one or more of the following techniques: 1) examination of pulp properties after extraction of soluble hemicelluloses with alkali, 2) comparison of pulps of various hemicellulose contents prepared under different cooking conditions, and 3) the use of a beater adhesive technique, i.e., addition of alkali-extracted hemicellulose to normal pulps or to the residues after extraction.

There are experimental difficulties associated with all three above approaches and these difficulties complicate interpretation of the results. Studies on the effects of hemicelluloses based on changes in hemicellulose content upon alkaline extraction of pulps are complicated by the action of alkali on the remaining fibrous material. McKenzie and Higgins (3) found that upon alkaline treatment, changes take place in the interfiber bonding

capacity of pulps deficient in hemicellulose and these changes are comparable to those which take place in normal pulps. Alkaline extraction also affects the remaining hemicelluloses and upsets the original hemicellulose-cellulose association in the fiber.

The comparison of pulps prepared with different pulping conditions yields only limited information concerning the effects of hemicelluloses. In a recent study, Thompson, Peckham, and Thode (5) studied carbohydrate changes and related physical effects throughout a wide range in pulping conditions. These authors concluded that in pulps prepared under such pulping conditions both the nature and distribution of hemicelluloses differ and that the papermaking properties of pulps reflect the different chemical treatments to which the pulps were subjected during pulping. Thus, comparisons of pulps prepared with different chemical treatments cannot distinguish effects due to the type and amount of hemicellulose from effects due to fiber degradation and modification.

Studies based on the use of hemicelluloses as beater adhesives have inherent difficulties also. The isolated hemicellulose polymer is unavoidably subjected to possible change during isolation. The original hemicellulose-cellulose association as it existed in the pulp cannot be duplicated either. The hemicelluloses sorbed by cellulose fibers are limited to the accessible sites which are believed to be predominantly on the external fiber surface. Obviously, the magnitude of any effect caused by a certain quantity of sorbed hemicellulose is not identical with that achieved when the same quantity of hemicellulose is distributed within the fiber structure.

Even with these inherent limitations, the beater adhesive technique is useful because it permits utilization of fully characterized hemicelluloses,

both natural and modified. The majority of investigators using the beater adhesive technique have been concerned with the quantity of hemicellulose added to pulp suspensions rather than the specific types and amount retained. Very little attention has been focused on the physical and chemical properties of the hemicellulosic materials used and the contributions these various properties may make to sorption of the polymers and to the physical properties of the cellulose substrate.

Thompson, Swanson, and Wise (6) made an initial study of the factors influencing the effectiveness of hemicelluloses as beater adhesives. They found the softwood hemicelluloses superior to those of the hardwood in improving the strength properties of handsheets. This difference was believed to be due to the higher mannan content of the softwood hemicelluloses. This work indicated the existence of a critical minimum degree of polymerization. A highly branched polymer, an arabinogalactan, proved to be ineffective as a beater adhesive. These authors did not determine retentions of the various hemicelluloses and noted that these differences in strength properties could result from differences in retention as well as differences in chemical composition and structure of the hemicelluloses.

Most (7) studied the sorption of slash pine hemicellulose fractions similar to those used by Thompson, Swanson, and Wise (6). These fractions were isolated from a slash pine chlorite holocellulose by successive extractions with 1, 4, 7, and 16% potassium hydroxide solutions. With this method of isolation, each fraction is unavoidably a mixture of hemicelluloses. The predominant hemicelluloses in softwoods are glucomannans with side branches of galactose units and xylans with side branches of other pentose units and 4-O-methylglucuronic acid.

Mannan contents of these fractions reflect glucomannan contents while pentosan and uronic anhydride values reflect the xylan content. The mannan content of the fractions increased and the uronic anhydride and pentosan contents decreased with increasing potassium hydroxide concentration. The specific sorption of the fraction isolated with 16% potassium hydroxide (high mannan, low pentosan and uronic anhydride contents) was nearly three times as great as that of the fraction isolated with 1% potassium hydroxide (low mannan, high pentosan and uronic anhydride contents). Most's work indicates that the contributions to paper properties observed by Thompson, Swanson, and Wise were due, at least in part, to different retentions of the various hemicellulose fractions. However, the conclusion that the differences in retentions were due entirely to mannan content is not justified because each fraction was a mixture and several variables differed among the various fractions.

The mechanism through which hemicelluloses contribute to papermaking properties of fibers is not fully understood. It is remarkable that a small amount of hemicellulose, chemically similar to cellulose, can produce significant increases in observed properties of cellulose pulps. Advancement of knowledge in this area will depend on further fundamental research to determine the exact chemical and physical differences between cellulose and hemicellulose and how these differences affect fibrous properties. The distribution and accessibility of hemicelluloses within the fiber structure appear to be important factors. The effect that the presence of hemicelluloses has on the hydrophilic nature of fibers, i.e., the ability of fibers to be hydrated, appears to be very important. The term hydration, used when the solvent is water, is a special case of solvation which is a specific interaction between ions and solvent molecules. There is little evidence that a true chemical hydrate is formed; however, it is a

well-established fact that hydration results in a plasticized and swollen cellulose fiber.

Swanson (2, 8) has discussed evidence that the swelling of fibers is closely connected with fiber bonding in papermaking operations. Elements which are to be bonded together must be brought within a few Angstrom units of one another so that forces of attraction can be effective. Thus, it is very important in papermaking to prepare the fibrous material so that intimate contact between fibrous elements can occur on a molecular scale. Better molecular contact between cellulose fibers can be achieved when the fibers are plasticized and swollen. Since paper is normally formed from a water suspension, the degree of fiber hydration achieved is an important property.

The hydroxyl groups of cellulose are primarily responsible for the pronounced affinity of cellulose for water. Bletzinger (9), Aiken (10), McKenzie and Higgins (11), and Harrison (12) have substituted hydrophobic groups (e.g., acetyl) into cellulosic pulps. At low degrees of substitution (D.S.) the affinity for water of the substituted celluloses was increased apparently due to an opening up of the cellulosic structure making more of the cellulosic hydroxyl groups available for hydration. As the D.S. was further increased, the number of free hydroxyls in the pulps was significantly decreased and this resulted in a decrease in the physical strength of handsheets. However, Aiken and Bletzinger showed that when these fibers of higher D.S. were beaten in an organic solvent which permitted appreciable swelling, molecular bonding occurred and the handsheets had good strength properties.

Walecka (13) and Talwar (14) substituted carboxymethyl groups (more hydrophilic than hydroxyls) into cellulose pulps and found that handsheets from these

low-D.S. carboxymethyl cellulose (CMC) pulps have higher physical strength properties than handsheets from the original pulp and achieve these increased strengths with less beating. Talwar found marked differences in the behavior of the substituted pulps when carboxyl group was changed from the sodium salt form to the acid form. The CMC pulp handsheets were formed in water and then solvent exchanged with dilute alkali, acid, or alum solution. In filtration resistance determinations, the pulp slurries were adjusted to selected values of pH or concentration with alkali, acid, or alum. Talwar undoubtedly achieved the sodium salt form with alkali; however, the treatments employed to attain the acid form were probably inefficient. Adjustment of slurry pH to acidic conditions must be accompanied with sufficient time to establish ion-exchange equilibrium when carboxyls within a pulp are to be changed from salt to acid form. In the sodium salt form, the CMC pulps showed much better dispersion characteristics, lower freeness values, higher filtration resistances, and increased sheet strength values. These results indicate that the particular ionic form of the carboxyls is an important factor in the behavior of pulps containing carboxyl groups.

Numerous investigators have hypothesized that hemicellulosic uronic acid carboxyls in wood pulps contribute measurably to fibrous properties; however, direct experimental evidence of the hypothesized effects has not been obtained. Wurz and Swoboda (15) and Jayme and von Köppen (16) advanced the hypothesis that the ability of sulfite pulps (and possibly kraft pulps of the angiosperms) to respond rapidly to beating is correlated to their polyuronide content. Saarnio (17) found a good correlation between the carboxyl content and the water adsorption and hydration properties of a series of bleached and unbleached sulfite pulps. However, the observed effects were not necessarily due entirely to the

presence of carboxyl groups because the total hemicellulosic content increased with increasing carboxyl content and this study was based on a comparison of fibers which had been subjected to various degrees of chemical treatment.

An experimental technique that will limit the major variable to a change in uronic acid carboxyl content is needed to obtain direct experimental evidence of the possible contributions by these carboxyls to the papermaking properties of fibers. McKee (18) partially reduced the 4-O-methylglucuronic acids of an isolated 4-O-methylglucuronoxylan to 4-O-methylglucose as indicated in Fig. 1. This diborane reduction technique suggests that one pulp could be prepared by sorption of a hemicellulose which contains unreduced uronic acid carboxyls and could be compared to a second pulp containing an equal sorbed quantity of the same hemicellulose after partial reduction of the uronic acid carboxyls. Such an experimental approach would require careful evaluation of any possible effects the hemicellulosic carboxyl content may have on the relative sorption of the two hemicellulose polymers.

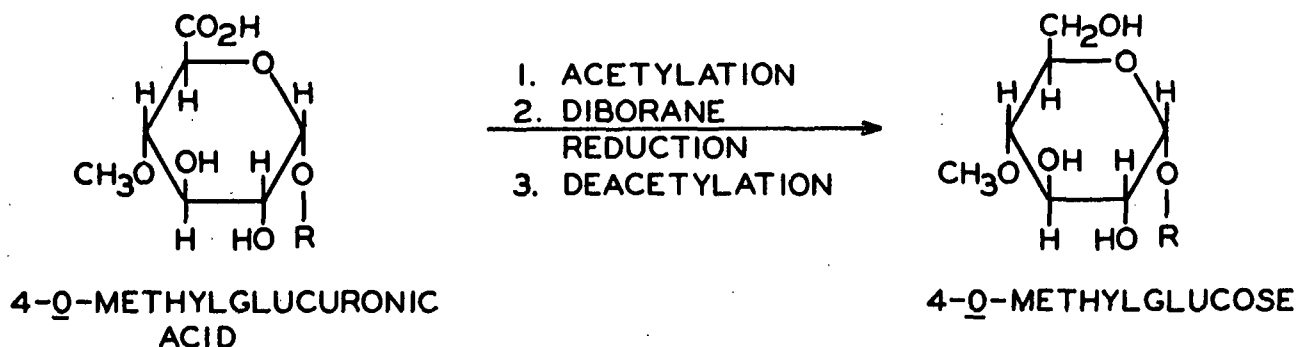


Figure 1. Diborane Reduction of 4-O-Methylglucuronic Acid

If these carboxyls do affect the affinity of hemicelluloses for water, it can be anticipated that reduction of the uronic acid carboxyls should reduce the solubility of a hemicellulose polymer in water. A reduction in solubility

leading to unequal retentions of the reduced and unreduced polymers on a cellulose substrate when water is the solvent must be considered since the qualitative rule (19) states that adsorbability increases when solubility decreases. The fact that an isolated hemicellulose polymer is made up of species of different molecular sizes must also be considered. Polymer sorption, in general, is molecular weight dependent and has been found to increase with increasing molecular weight at small molecular weights (20). However, the data in the particular case of hemicellulose sorption on cellulose pulps are limited. The possibility that the reduction technique could alter the molecular weight distributions and subsequently, the relative sorptions of the reduced and unreduced polymers had to be considered also.

The experimental program of this thesis was designed to test the hypothesis that the uronic acid carboxyls affect the sorption of a hemicellulose and in turn influence the papermaking properties of pulps. The investigation includes evaluation of effects involved in sorption and methods of overcoming undesirable sorption effects as well as evaluation of effects on fibrous properties. The fibrous properties selected for examination; e.g., filtration resistance, response to beating, and handsheet properties, are those which are considered important papermaking properties and could be expected to be a function of pulp hydration. If the uronic acid carboxyls do increase the ability of a pulp to hydrate, a pulp of higher uronic acid content should have a greater filtration resistance, should respond more rapidly to beating, and should have improved handsheet strength properties.

EXPERIMENTAL

HEMICELLULOSE ISOLATION

Two seasoned, peeled sprucewood logs were obtained from the Interlake Division mill of Consolidated Papers Inc., Appleton, Wis. A portion of each bolt was chipped, screened, and pulped with laboratory equipment. An alkaline sulfite (sulfide) pulping procedure was utilized as outlined by Peckham and Van Drunen (21). The experimental details are presented in Appendix II. A 4-O-methylglucuronoarabinoxylan was isolated from this pulp as outlined by Thompson, Peckham, and Thode (5). The hemicellulose was extracted from the pulp with 5% sodium hydroxide at room temperature. The alkaline extract was acidified immediately to minimize any possible alkaline degradation and was then concentrated and added to two volumes of 95% ethanol to precipitate the extracted hemicellulose.

The light tan precipitate was bleached with sodium chlorite-acetic acid under relatively mild conditions and most of the color was removed. The precipitate was solvent exchanged with 95% ethanol, absolute ethanol, and petroleum ether (30-60°C.) and was then dried in vacuo over calcium chloride and paraffin.

Analysis of the hemicelluloses follows: yield (ash and moisture-free basis), 1.3% based on oven-dry wood; moisture, 9.28%; sulfated ash, 1.73% as sodium; intrinsic viscosity, 0.705 in 0.5M cuene; uncorrected carbon dioxide, 2.77%. Qualitative chromatography indicated the presence of large amounts of xylose, lesser amounts of uronic acid and arabinose, and trace amounts of galactose, glucose, and mannose. Quantitative chromatography and corrected

carbon dioxide data indicate the hemicellulose has the following sugar ratio: 8:1:1, xylose:arabinose:4-O-methylglucuronic acid. The hemicellulose is believed to be similar to the 4-O-methylglucuronoarabinoxylan reported by Thompson, Peckham, and Thode (5).

REDUCTION OF 4-O-METHYLGLUCURONOARABINOXYLAN

ACETYLATION

With the exception of a few grams saved for future reference, the entire hemicellulose sample was acetylated according to a procedure outlined by Carson and MacLay (22). The acetylated polymer was difficult to isolate from the reaction mixture because it formed a soft gel which was difficult to filter and solvent exchange. This problem was eliminated once the gel was broken with chloroform. The acetate was removed as a well-defined precipitate in water suspension when the chloroform was evaporated in a vacuum evaporator. The acetate was solvent exchanged with 95% ethanol, absolute ethanol, and petroleum ether (30-60°C.) and was then dried in vacuo over calcium chloride and paraffin.

Analysis of the acetate follows: moisture, 2.25%; sulfated ash, 0.07% as sodium; apparent acetyl (23), 36.6% (ash, moisture, and acid-free basis).

A portion of the acetate was saved for future reference, and a portion was used to prepare a reduced polymer. The remaining acetate (80 g.) was deacetylated in 2 liters of 5% potassium hydroxide (45 minutes at 55-60°C.). The solution was filtered and acidified with acetic acid. The deacetylated hemicellulose (hereafter referred to as GAX) was precipitated with 2 volumes of 95% ethyl alcohol, filtered, washed with 95% ethyl alcohol, and the particle size reduced in the Waring Blendor. The GAX was solvent exchanged with 95%

ethanol, absolute ethanol, and petroleum ether (30-60°C.) and was then dried in vacuo. Analysis of the GAX follows: moisture, 5.54%; sulfated ash, 8.14%; carbon dioxide, 2.64%; intrinsic viscosity in 0.5M cuene, 0.857. The methoxyl content, 1.40% OH_2O , was determined (according to Institute Method 18) on a portion which had been deionized with Amberlite resin IR-120 and then freeze-dried.

GASEOUS DIBORANE REDUCTION

Initially it was planned to reduce the GAX carboxyls with the diborane reduction technique as described by McKee (18). This technique involves generation of diborane in situ by the addition of boron trifluoride etherate in bis (2-methoxyethyl) ether ("diglyme") to a solution of the compound and sodium borohydride in diglyme solution. However, Thompson (24) discovered that the technique used by McKee produces a by-product which had previously been overlooked. Ross (25) found evidence that the by-product was produced by ethylation of the xylan chain.

The exact nature of the artifact and any effect that it might have in this study were unknown. Therefore, a series of experiments were undertaken to achieve reduction of the GAX without production of the artifact. This was done through the application of a gaseous diborane technique. The reduction apparatus shown in Fig. 2 is essentially that used by McKee, the exception being separate diborane generation and reaction flasks. Tetrahydrofuran was selected for the reaction medium because the GAX acetate was more highly swollen in this solvent than in diglyme. Also, the lower boiling point of tetrahydrofuran is advantageous in the recovery of the reduced polymer from the reaction mixture. Brown and Subba Rao (26) reported that diborane was more soluble in

tetrahydrofuran than in diglyme, but no significant difference was observed using either solvent. Brown and Tierney (27) found diborane to be sorbed by sodium borohydride in solution, forming the complex $\text{NaBH}_4 \cdot \text{BH}_3$. These authors achieved a smoother, more regular evolution of diborane by avoiding the presence of an excess of NaBH_4 in solution. Thus, they preferred to generate B_2H_6 by the slow addition of NaBH_4 in diglyme to BF_3 etherate in diglyme. Nonetheless, their results showed B_2H_6 generation was very nearly quantitative when the above procedure was reversed. In the present work, the reverse procedure (addition of BF_3 etherate in diglyme to NaBH_4 in diglyme) was chosen due to convenience and because this technique limits the possible entrance of BF_3 etherate vapors into the reaction flask. The orienting experiments showed that no artifact was produced by this technique with or without NaBH_4 in the reaction flask. Therefore, NaBH_4 was employed in the reaction flask because: 1) due to its alkaline nature it prevented high acidity (B_2H_6 is a Lewis acid) and the possibility of hydrolysis, and 2) it was believed that the formation of the $\text{NaBH}_4 \cdot \text{BH}_3$ complex would help prevent loss of excess B_2H_6 from the reaction mixture. It was shown that the GAX acetate tended to form a gel structure in diglyme or tetrahydrofuran (the effect seemed greater in the latter) as the reaction proceeded. This gel formation lowered the extent of reduction, but its occurrence could be prevented by adequate agitation.

Following are the conditions used to prepare the reduced GAX (GAXR): The GAX acetate (26.0 g.) was dispersed in tetrahydrofuran (1600 ml.) and stirred for 3 hours. At this point, the acetate was not in solution, but did appear to be highly swollen. Sodium borohydride (5 g.) was added to the reaction flask and also to the B_2H_6 generation flask (30 g. in 500 ml. diglyme). The entire reduction train was swept with nitrogen (10 l./hr.) and BF_3 etherate

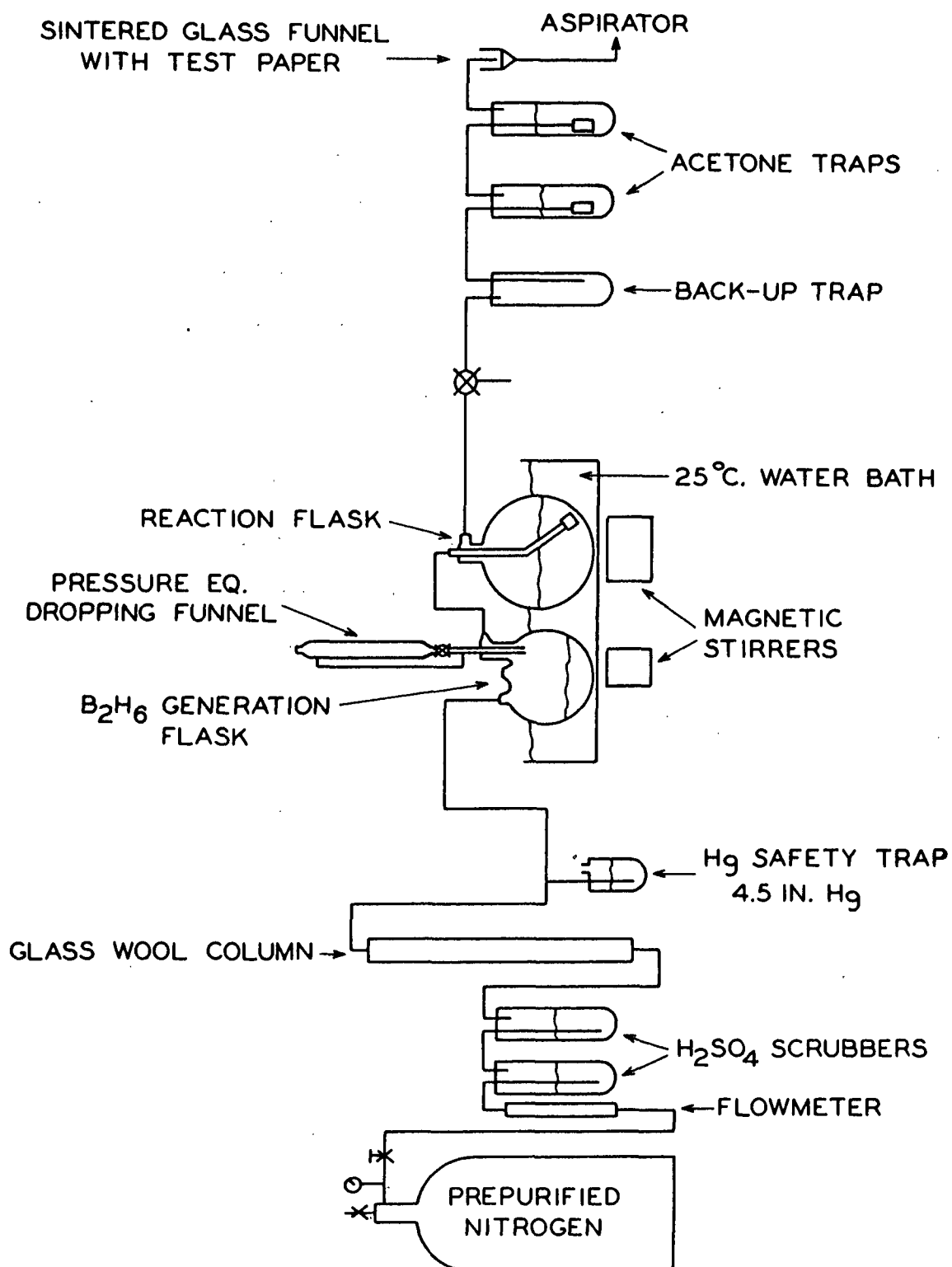


Figure 2. The Reduction Apparatus

(90 ml. in 50 ml. diglyme) was added dropwise over a 20-minute period. The nitrogen flow was continued for another 30 minutes. The reaction flask was stoppered lightly and stirring was continued overnight. The reaction train was swept with nitrogen the following morning, and an additional 30 g. NaBH_4 was added to the generation flask. BF_3 etherate (90 ml. in 40 ml. diglyme) was added dropwise over a 30-minute period. The nitrogen flow was continued for an additional 20 minutes. The mixture was then stirred intermittently for one hour. The reaction was stopped by pouring the reaction mixture into 200 ml. water. The pH at this point was 6.0. The reduced acetate was precipitated by the addition of 2 volumes of 95% ethyl alcohol, and separated by centrifugation. The supernatant liquid, after careful centrifugation, gave a negligible amount of residue upon evaporation of the tetrahydrofuran and addition of several more volumes of ethanol. The acetate was deacetylated by heating in 800 ml. 5% potassium hydroxide for 45 minutes at 55-60°C. The alkaline solution was filtered and acidified with acetic acid to pH 5. GAXR was precipitated from the filtered solution by the addition of 2 volumes of 95% ethyl alcohol, filtered, washed with 95% ethanol, and its particle size reduced in the Waring Blendor. After additional washing with 95% ethanol, the GAXR was solvent exchanged with absolute ethanol and petroleum ether (30-60°C.) and dried in vacuo over calcium chloride and paraffin. A second batch of GAXR was prepared from 15.3 g. GAX acetate under comparable conditions and was combined with the first batch of GAXR.

The analysis of the GAXR follows: moisture, 6.92%; sulfated ash, 7.4%; carbon dioxide, 1.37%; yield during reduction, 90%; intrinsic viscosity in 0.5M cuene, 0.867. The methoxyl content, 1.40% CH_3O , was determined according to Institute Method 18 on a portion which had been deionized with Amberlite resin IR-120 and then freeze-dried. Employing the carbon dioxide data and the

correction factor, 0.50%, Yundt (28) reported for xylan, the reduction is calculated to be 60%. The 4-O-methylglucose content (resulting from the reduction of 4-O-methylglucuronic acid) of the GAXR hydrolyzate was estimated with a chromatographic technique outlined by Ross (25). The results indicated the presence of about 6% 4-O-methylglucose which is the order of magnitude anticipated from the carbon dioxide data. The solubility of GAXR in water was much less than that observed with GAX. GAXR was more difficult to disperse in water and formed cloudy solutions.

MOLECULAR CHARACTERIZATION OF REDUCED AND UNREDUCED POLYMERS

The number average molecular weights, \overline{M}_n , of the reduced and unreduced polymers were determined with a high-speed osmometer, Model 501 manufactured by Mechrolab Inc., by Swenson and Schmitt (29). The membrane employed, Polypore Solvent Resistant Membrane Filter type 27 G supplied by the Gelman Instrument Co., is the densest (ultracella allerfeinst) membrane available. Measurements were made using solutions of the fully acetylated polymers in trifluoroethanol (TFE) at 37°C. The instrument's temperature controller is rated at $\pm 0.001^\circ\text{C}$. \overline{M}_n values for these two polymers were also determined with an osmometer of the Zimm-Meyerson type and these experimental details are presented in Appendix II. The values determined with the high-speed osmometer are believed to be more accurate than those determined with the Zimm-Meyerson type due to the rapid determination times in the former which minimizes the possibility of polymer degradation. Plots of the osmotic height, \overline{H} , divided by weight concentration, \overline{w} , as a function of \overline{w} for the reduced and unreduced polymers determined in the high-speed osmometer are shown in Fig. 3.

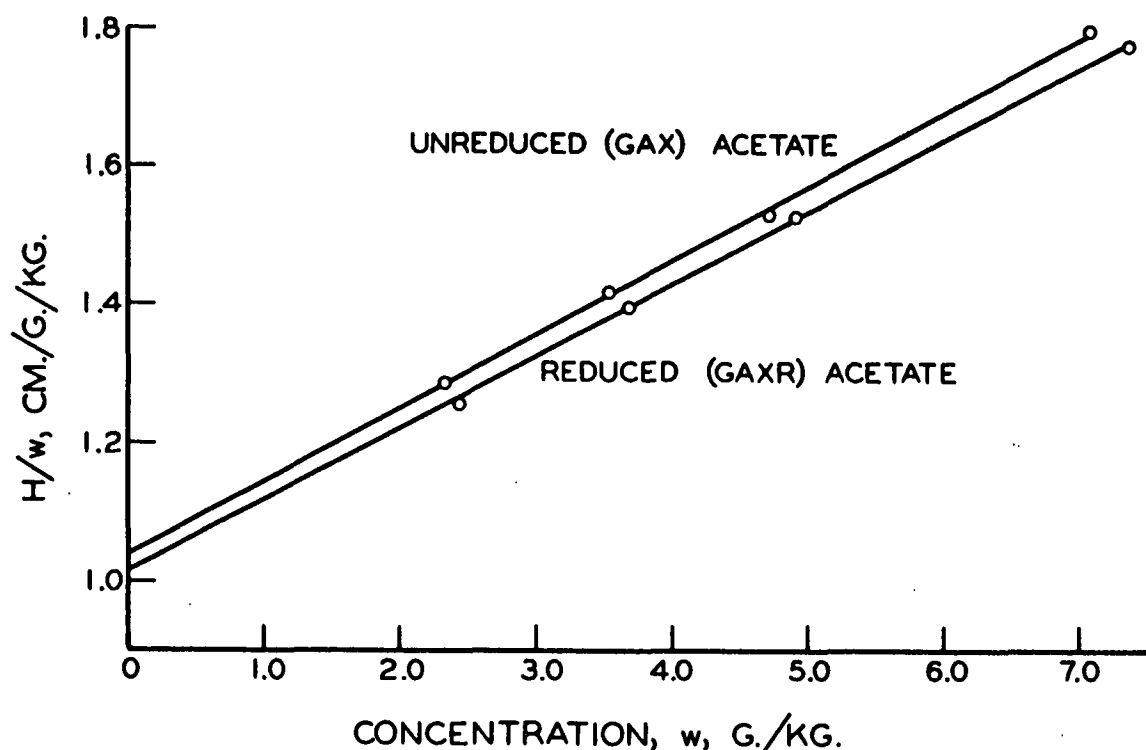


Figure 3. Osmotic Pressure Graph of Reduced and Unreduced 4-O-Methylglucuronocarabinoxylan Acetates

The number average molecular weights and degrees of polymerization (D.P.) calculated from osmotic pressure data are presented in Table I. The number average molecular weights of the reduced and unreduced polymers are quite similar. The degrees of polymerization were estimated assuming an average monomer weight equal to 137 for the unreduced polymer (GAX) and 135 for the reduced polymer (GAXR) based on the determined ratio of sugars.

TABLE I

NUMBER AVERAGE MOLECULAR WEIGHTS AND DEGREES OF POLYMERIZATION OF THE REDUCED AND UNREDUCED POLYMERS

	GAX	GAXR
$(\frac{H}{w})_0$	1.040	1.015
\overline{M}_n (acetate)	25,280	25,910
\overline{M}_n (deacetylated)	16,030	16,530
Degree of polymerization	117	121

Several attempts to accomplish fractionation of the GAX polymer from a water solution by the addition of alcohol were unsuccessful. The primary reason for failure of these attempts is believed to be the precipitant-solvent system since the GAX polymer was found to be extremely soluble in water-alcohol solutions.

Samples of the polymers used in this study were presented to Swenson (29) for use in a study on the molecular properties of hemicelluloses. In a pilot fractionation, he used petroleum ether (60-110°C.) to precipitate GAX acetate from a methylene chloride/methanol (95/5) solution. Eighteen fractions representing about 90% of the starting material were donated for use in this investigation.

Intrinsic viscosities were determined for most of the fractions in TFE. The solution in the viscometer was retained and the recovered polymer was used for methoxyl determinations. Methoxyl determinations were done according to Institute Method 18 with the exceptions that 0.0102N sodium thiosulfate was used and samples were not wrapped in cigarette papers. Instead, the samples were dissolved in methylene chloride/methanol (95/5) and transferred to tabs (1 x 3 cm.) of no. 17 Whatman filter paper which previously had been dried in vacuo over phosphorus pentoxide (25.5 in Hg, 70°C.) and weighed (semimicro balance). The tabs and polymers were redried and reweighed to obtain polymer weights. Blank tabs were submitted to the same treatment including methylene chloride/methanol without polymer. These results are presented in Table II.

The methoxyl values were higher than expected and suggest that solvent sorption by the polymer probably occurred. The blank tabs were also treated with solvent to offset the error due to solvent adsorption on the paper tab; however, the polymer itself may have retained solvent. The results may have

TABLE II

GAX ACETATE FRACTIONATION DATA

No.	Fraction Weight, mg.	$[\eta]$ in TFE, 30°C.	CH ₃ O, %
1	11.4	1.013	1.42
2	26.2	--	1.09
3	23.4	--	1.19
4	20.0	0.910	2.07
5	28.4	--	---
6	25.5	0.885	0.80
7	23.7	0.880	2.20
8	22.9	0.847	2.92
9	19.9	0.830	0.75
10	23.5	--	1.40
11	20.8	0.762	0.95
12	14.9	0.702	2.18
13	24.5	--	1.05
14	16.8	0.542	0.98
15	12.9	0.413	2.02
16	12.9	0.390	1.15
17	14.0	0.300	1.38
18	17.0	0.110	1.46

been more accurate if all the paper tabs had been humidified and redried after solvent was added. Although the accuracy is relatively low, these data indicate a random substitution of 4-O-methylglucuronic acid along the polymer chain without any correlation to molecular weight.

The intrinsic viscosity data suggest that the polymer has a fairly narrow molecular weight distribution. The accumulative weight per cents of the fractions were plotted as a function of intrinsic viscosity. A differential weight distribution function was calculated by measuring slopes of this plot at selected values of intrinsic viscosity. These differential weight distribution functions are plotted as a function of intrinsic viscosity in Fig. 4.

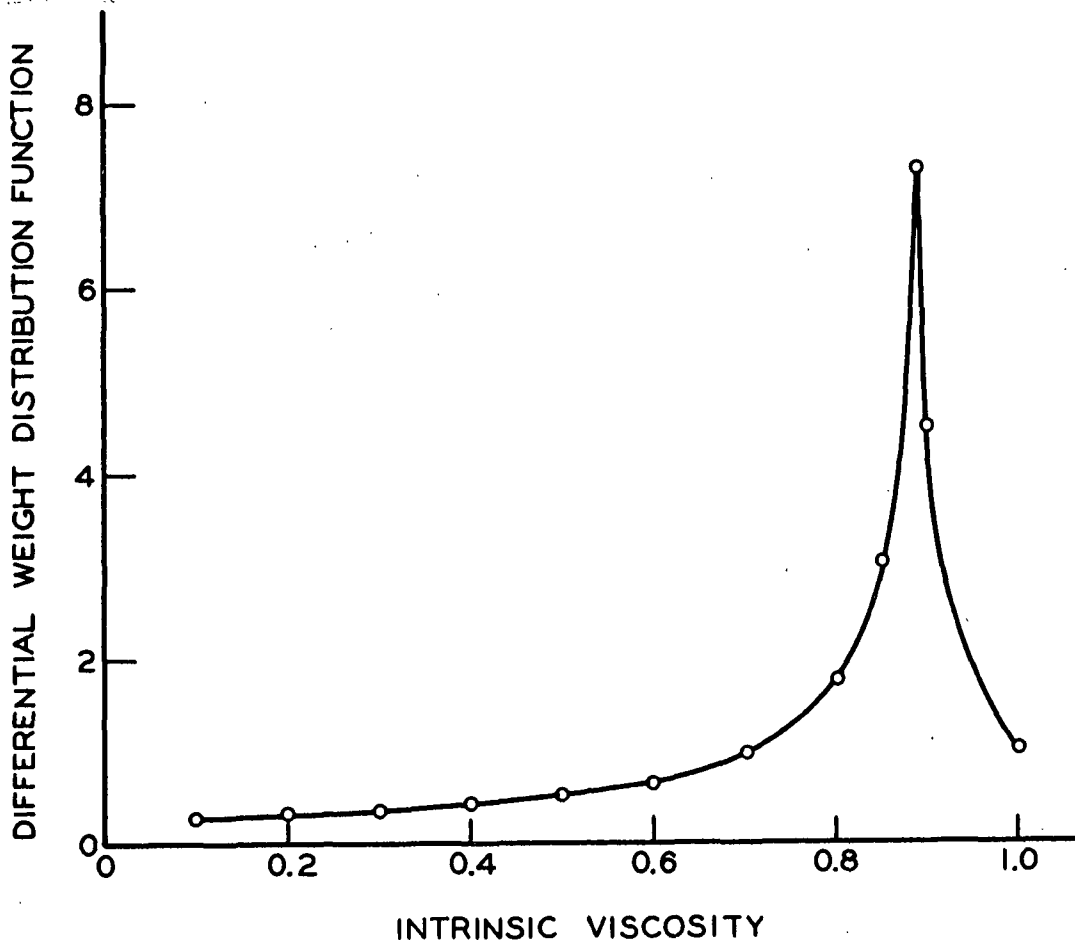


Figure 4. Intrinsic Viscosity Distribution of GAX Acetate

A weight average to number average molecular weight ratio, $\frac{M_w}{M_n}$, can be estimated from the fractionation data. The definitions of the above quantities may be written (30)

$$M_w = \sum w_i M_i \quad (1)$$

$$M_n = 1 / \sum (w_i / M_i) \quad (2)$$

where w_i is the weight fraction of species with molecular weight M_i . Assuming that intrinsic viscosity, $[\eta]_i$, is a direct measure of M_i , the ratio of Equations (1) and (2) may be written

$$M_w / M_n = \left[\sum (w_i [\eta]_i) \right] \left[\sum (w_i / [\eta]_i) \right] \quad (3)$$

Using Equation (3) and the above fractionation data, the $\frac{M_w}{M_n}$ ratio was calculated to be 1.33. Swenson and Schmitt (29) determined $\frac{M_w}{M_n}$ of the GAX acetate by light scattering to be 32,300. The ratio of this value to the value of $\frac{M_n}{M_n}$ determined by osmotic pressure is 1.28. Both ratios indicate a narrow molecular weight distribution and the apparent agreement of these two ratios suggests that the individual fractions were very nearly homogeneous. Swenson and Schmitt are continuing work in this area. A narrow molecular weight distribution for birch xylan has been reported by LeBel and Goring (31).

PREPARATION OF THE COTTON LINTERS SUBSTRATE

Cotton linters were chosen for the cellulose pulp substrate because they contain only negligible amounts of hemicellulose. This was desirable since it increases the sensitivity of sugar chromatography used to measure retention of the sorbed hemicelluloses. Shriver (32) reported that unbeaten cotton linters

pulp was a poor substrate in the sorption of water-soluble cellulose ethers. However, sorption was significantly increased when a beaten cotton linters pulp was used.

The cotton linters used in this study were previously stored in dry lap form in the pulp lab. Pulp samples were soaked in water for at least four hours before refining. The cotton linters pulp was refined under standard conditions for 90 minutes in a Valley laboratory beater. This treatment was selected because it produced a classified pulp which had sufficient surface area for sorption and a desirable level of filtration resistance. The refined pulp was processed through the Bauer-McNett classifier with the 20-, 35-, 65-, and 150-mesh screens. The fraction passing the 150-mesh screen was discarded. The beaten, classified cotton linters pulp, hereafter referred to as CL pulp, was washed with methanol, centrifuged, and stored.

Figure 5 is a photomicrograph of the beaten and classified cotton linters pulp used in this study. There is considerable fibrillation, but not an excessive amount. This loosening of the external fiber surface exposes a significant amount of the internal fiber structure as potential sorption sites. Classification produced a pulp relatively free of fiber debris. Fiber debris is undesirable because it has a higher specific surface area than does the whole fibers and would result in an inefficient retention of hemicellulosic beater adhesives.

SORPTION STUDIES

SORPTION APPARATUS

Sorption samples were carefully sealed in 32-oz. bottles and rotated in a constant temperature ($30 \pm 0.05^{\circ}\text{C.}$) bath. The rotator consists of two parallel

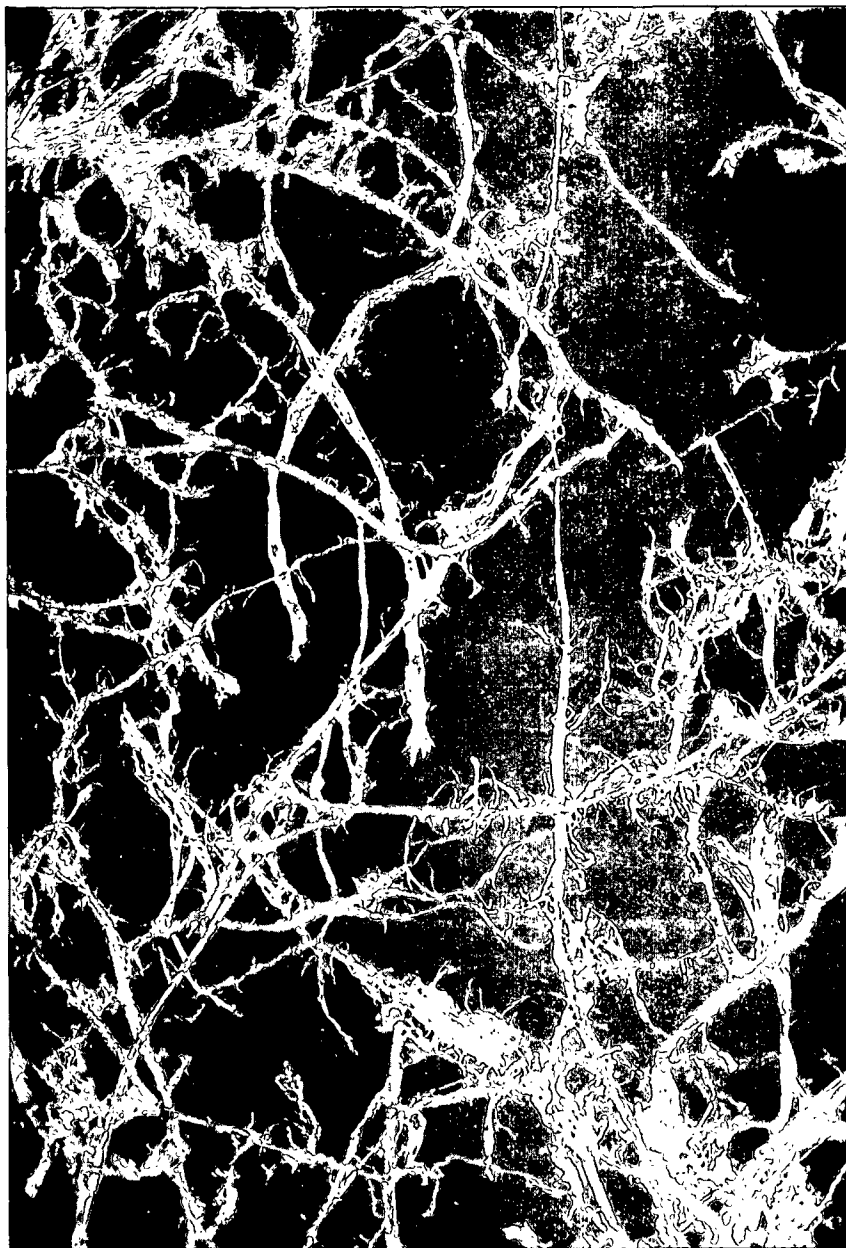


Figure 5. Photomicrograph of Beaten, Classified
Cotton Linters (65X)

metal plates independently mounted on a common shaft. The periphery of both plates is notched and fitted with spring clamps to accommodate the bottles about five inches away from the shaft. The shaft is driven at a constant speed of 10 revolutions per minute. If one plate is advanced a few degrees in relation to the other, the axis of the sorption bottle is not parallel to the axis of the plates. This causes an end-to-end agitation as well as circumferential motion.

PREPARATION OF GAX AND GAXR PULPS

The GAX and GAXR pulps were prepared by sorption of GAX (unreduced hemicellulose) and GAXR (partially reduced hemicellulose), respectively, on the beaten and classified cotton linters pulp (CL pulp). The sorption conditions selected were: 2.0 g. pulp/100 g. solution, 5.0% polymer based on pulp, solution 0.02N hydrochloric acid, constant temperature $30 \pm 0.05^{\circ}\text{C.}$, and a 48-hour sorption time. Most (7) demonstrated that hemicellulose sorption on cellulose fibers in water is very rapid initially, but decreases to a very low rate after about 10 hours. This low rate continued for several days and indicated that true equilibrium conditions, if attainable, would require very long sorption times. Thus, a 48-hour sorption time represents a "pseudo-equilibrium" condition. The pulp samples (16.0 g. in 500 ml. water) were placed in sorption bottles and rotated in the bath overnight. The GAX and GAXR polymer solutions (0.800 g. polymer in 200 ml. water) were shaken intermittently and left at room temperature overnight. These solutions and additional required water were added to the pulp samples in the sorption bottles. Sufficient standard hydrochloric acid was then added and the bottles were rotated for 48 hours. After sorption, the pulp samples were filtered on coarse fritted glass filter funnels and washed thoroughly with distilled water followed by methanol. Preliminary experiments showed that there

was no detectable quantity of hemicellulose in the filtrate once the pulp washings were no longer acidic.

Polymer retentions were determined chromatographically. The Saeman (33) technique was adopted with modifications as described in Appendix II. This technique involves total hydrolysis of the pulp with sulfuric acid, isolation of the individual sugars by paper partition chromatography, and colorimetric determination of the sugars. Xylose recovery factors were determined for the reduced and unreduced polymers and were used to calculate polymer retentions on the prepared pulps.

The polymer retention values are shown in Table III. When the sorption solvent was 0.02N hydrochloric acid, the retentions of the two polymers were very similar indicating complete suppression of charge effects on the sorption of the polymers. The retention of the GAXR polymer is just slightly greater than that of the GAX polymer. In the absence of hydrochloric acid, the retention of the unreduced polymer, GAX, was only about half the retention obtained with the reduced (60%) polymer, GAXR.

TABLE III

POLYMER RETENTIONS ON BEATEN, CLASSIFIED COTTON LINTERS PULP

Polymer	Sorption Solvent	Polymer Retention, mg./g. pulp
GAX	0.02N HCl	36.2
GAXR (60% reduced)	"	37.2
GAX	water	9.1
GAXR (40% reduced)	"	12.0
GAXR (60% reduced)	"	16.1

The 40% reduced GAX obtained in a preliminary experiment was only slightly less soluble than the unreduced polymer. With water as the sorption solvent, polymer retention of this 40% reduced polymer was greater than that of the unreduced polymer, but less than that of the 60% reduced polymer. This result is further demonstration of the effect of the carboxyls on the solubility and sorption of the hemicellulosic polymers.

NATURE OF POLYMER NOT SORBED

The GAX and GAXR polymers remaining in the supernatant liquid after sorption, GAXS and GAXRS, respectively, were isolated. The prepared pulps were filtered on a sintered glass funnel and washed thoroughly with distilled water. The combined filtrates and washings were ion exchanged successively with Amberlite resins IRA-400 (anionic) and IR-120 (cationic). The deionized solutions were concentrated in a conventional vacuum evaporator and freeze-dried.

Methoxyl content of the GAXS polymer was determined (Institute Method 18) as a measure of uronic acid carboxyls. The methoxyl content of the GAXS polymer was 1.49% CH_3O . This is very similar to the value 1.40% CH_3O , which had been determined for the GAX and GAXR polymers again indicating a random distribution of the uronic acids on various molecular species. Methoxyl content of the GAXRS polymer was not determined because methoxyls may originate from both 4-O-methylglucose and 4-O-methylglucuronic acid in the reduced polymer and does not reflect the uronic acid carboxyl content.

The above results indicate that with the sorption conditions used there is little, if any, tendency for preferential sorption of fractions of lower carboxyl content, leaving a fraction of higher carboxyl content in solution.

This conclusion is supported through the determination of pulp carboxyl content with methylene blue sorption reported later in this study.

GAXS and GAXRS polymer samples were hydrolyzed with sulfuric acid. Qualitative chromatograms indicated the presence of a very small amount of glucose. The ratio of xylose and glucose was analytically determined and indicates that the amount of glucose present is less than 2%. Cellulose was not appreciably solubilized in these sorption experiments, whereas other workers (7) have reported significant quantities of cellulose in the supernatant liquid. The conditions used in this experiment must have suppressed peptization of shorter chain glucans from the fibers.

The intrinsic viscosities of the GAXS and GAXRS polymers were measured in 0.5M cuene and were considerably lower than those measured for the original polymers. However, it was shown that samples of the original polymers which had been deionized (IR-120 only), and freeze-dried also had considerably lower intrinsic viscosities than the original polymer. A recheck of the original polymers (which had been stored in the salt form) showed that these polymers had retained their originally high viscosities. A series of experiments undertaken to explain this phenomenon are shown in Fig. 6. Neither freeze-drying nor solvent exchange and in vacuo drying appear to affect intrinsic viscosity significantly.

Thus, the observed decrease in intrinsic viscosity by the deionized, freeze-dried samples seems to be due to either partial selfhydrolysis of the polymers in the acid form or some other effect caused by the deionization treatment. There is a small loss of polymer due to sorption on the resin, but this loss cannot account for such a large change in viscosity. Selfhydrolysis appears to

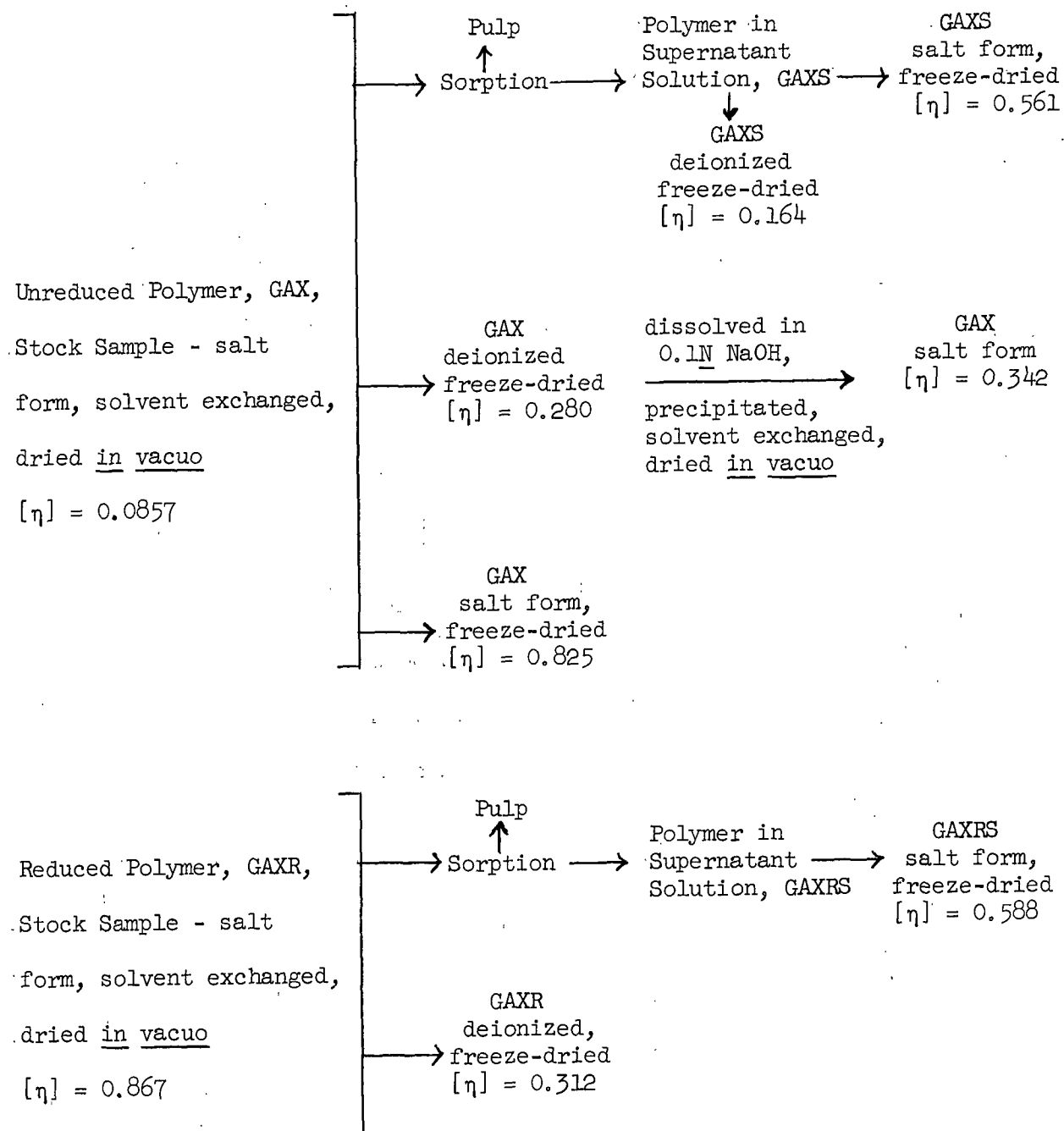


Figure 6. Flow Chart of Polymer Intrinsic Viscosity Determinations

be the most plausible assumption. The intrinsic viscosity data for the polymers isolated in the free acid form could not be used.

Samples of the GAXS and GAXRS polymers were then isolated from the supernatant liquid without ion exchange. The combined filtrates and washings were titrated to pH 6.0 with standard sodium hydroxide. The neutralized solutions were concentrated in a conventional vacuum evaporator and freeze-dried.

Samples of GAX and GAXR polymers were treated exactly as in preparation of GAX and GAXR pulps except there was no pulp in the sorption bottles. These solutions were titrated and treated exactly as the supernatant liquids above.

These four polymer samples had high ash contents. Thus, samples of known ash-free weight were repeatedly extracted with 80% methanol to reduce the ash content. After evaporation of excess alcohol from the residues, the samples were dissolved in a measured quantity of water and then an equal volume of 1.0M cuene was added producing a 0.5M cuene solution for the intrinsic viscosity measurements presented in Table IV. The GAXR intrinsic viscosities are slightly greater than the corresponding ones for GAX in both of these cases and for the original polymers.

TABLE IV

INTRINSIC VISCOSITIES OF POLYMERS IN SUPERNATANT SORPTION SOLUTIONS

Polymer	Sorption Conditions	
	Solvent	Pulps Present
GAX	0.02N HCl	yes
GAXR	"	"
GAX	"	no
GAXR	"	"

0.561

0.588

0.860

0.890

Apparently, preferential sorption of higher molecular weight material occurred since the viscosities of the polymers remaining in the supernatant solution after sorption were much lower than the original polymers, whereas the polymers subjected to sorption conditions without pulp experienced only a slight increase probably due to slight losses during isolation. Since viscosity is an additive property, the intrinsic viscosities of the polymer portions sorbed were calculated to be 0.964 for the GAX polymer and 0.969 for the GAXR polymer. This corresponds to degrees of polymerization of 132 and 135, respectively.

PULP CARBOXYL CONTENT BY METHYLENE BLUE SORPTION

On the basis of an investigation on the sorption of methylene blue from buffered solutions by cotton cellulose and oxycellulose, Davidson (34) concluded that the dye can be taken up by carboxyl groups and by hydroxyl groups. The contribution to the total sorption made by hydroxyl groups is negligible with oxycelluloses of high carboxyl content, though it may constitute an important fraction of the total sorption with materials of low carboxyl content, such as an unmodified cotton cellulose, in equilibrium with methylene blue solutions of relatively high concentrations. The sorption by carboxyl groups is a cation-exchange reaction, and as such it is influenced by the concentrations of methylene blue ions, hydrogen ions, and any other ions that may be present in the dye solutions. Sodium and potassium ions decrease the sorption of dye since they compete with the methylene blue ions, but their effect is small unless their concentration is high compared with that of the methylene blue ions.

Wilson and Mandel (35) published a recommended methylene blue sorption procedure for the determination of carboxyls in pulps. A known quantity of pulp is permitted to reach equilibrium with a known quantity of standard methylene blue

chloride solution (buffered with barbituric acid) and the optical density of the supernatant liquid is measured at 6750 Å. to determine the amount of methylene blue not sorbed by the pulp. The quantity of methylene blue chloride sorbed, representing the carboxyl content, is determined by difference.

The methylene blue sorption procedure presented by Wilson and Mandel was used with slight modification for the determination of carboxyl groups in the GAX, GAXR, and CL pulps. The procedure was modified by using 0.1 millimolar methylene blue solutions rather than 0.2 millimolar to increase the sensitivity of the test. There is reasonable agreement between the pulp carboxyl contents determined by methylene blue sorption and those calculated from the polymer retentions and the corrected carbon dioxide data for the polymers. These data are presented in Table V.

TABLE V
PULP CARBOXYL CONTENTS

Pulp	Carboxyl Content, millimoles COOH/100 g.	
	Methylene Blue Sorption	Calculated From Polymer Retention
GAX	2.26	2.06
GAXR	1.04	1.04
CL	0.30	--

FILTRATION RESISTANCE

The particular ionic nature of the uronic acid carboxyls in the sorbed hemicelluloses can be expected to be important in measuring filtration resistances of the GAX, and GAXR pulps since the sodium salt form of carboxyl groups is more hydrophilic than the free acid form. The carboxyl groups of the sorbed

hemicelluloses are in the free acid form since sorption was accomplished during a 48-hour period in 0.02N hydrochloric acid. Thus, a treatment had to be selected to prepare the sodium salt of the uronic acid carboxyls.

Talwar (14) used sodium hydroxide at pH 9.0, to prepare the sodium salt form of CMC pulps. However, sodium hydroxide would be expected to promote desorption of the sorbed polymers. Sodium bicarbonate was selected as a reagent of expected milder action.

Each pulp was dispersed (14.0 g. in 2 liters distilled water) in the standard disintegrator (300 counts). The pH of the resulting slurry was adjusted to 8.0 with a solution of sodium bicarbonate. The slurry was allowed to stand overnight before deaerating for filtration resistance and compressibility measurements. The cotton linters control pulps were placed in 0.02N hydrochloric acid and rotated for 48 hours in the sorption bath. Subsequent treatment was identical to that received by the GAX and GAXR pulps.

Ingmanson and co-workers (36, 37) have shown that the filtration resistance of relatively dilute slurries of a compressible material, such as cellulose fibers, in the streamline region of flow may be expressed as,

$$R = A^2/\mu C(dV/d\theta)^2 \quad (\Delta P_f/\theta) = B(\Delta P_f^2/\theta) \quad (4)$$

where \underline{R} is specific filtration resistance, \underline{B} is constant for a given constant-rate filtration and is equal to $\underline{A}^2/\mu \underline{C}(\underline{dV}/\underline{d\theta})$, (\underline{A} is the cross-sectional area of the fibrous bed, μ is the viscosity of water at the temperature of measurement, \underline{C} is the consistency of the slurry, and $\underline{dV}/\underline{d\theta}$ is the flow rate), $\Delta \underline{P}_f$ is the frictional pressure drop, and θ is time. Thus, filtration resistance may be calculated precisely from experimentally determined quantities.

Figure 7 shows that the pulp containing the unreduced polymer, GAX (sodium salt form), has a greater filtration resistance than does the pulp containing the reduced polymer, GAXR (sodium salt form). Both the GAX and GAXR pulps have greater filtration resistances than does the cotton linters control pulp, CL (sodium salt form).

The next experiment was made to check the hypothesis that the sodium salt form is more hydrophilic than the acid form. The filtration resistance of each of the three pulps in the acid form was determined without titrating the pulps to pH 8.0 with sodium bicarbonate. Figure 7 shows that all three pulps have a lower filtration resistance in the acid form than in the sodium salt form. The data for the GAX and GAXR pulps (acid form) form a common curve that lies slightly above the curve for the cotton linters (acid form).

Filtration resistance of each of the three pulps was measured at three beating intervals (10, 20, 30 min.) in the Jokro mill. Samples (14 g.) of GAX, GAXR, and CL pulps were washed with distilled water, the pH adjusted to 8.0 with sodium bicarbonate, and the total weight adjusted to 233 g. (6% consistency). After beating, each sample was dispersed 300 counts in the standard disintegrator and left overnight before determining filtration resistance and compressibility. Figures 8-10 show that the relative ranking of GAX, GAXR, and cotton linters pulps (all in sodium salt form) in Fig. 7 is maintained. In Fig. 11, filtration resistances of these three pulps are presented as a function of beating time. The values for filtration resistance were arbitrarily chosen at a pressure drop of 50 cm. water.

Filtration resistances were also determined for the GAX and GAXR pulps in the acid form at thirty minutes' beating time. The conditions of beating were

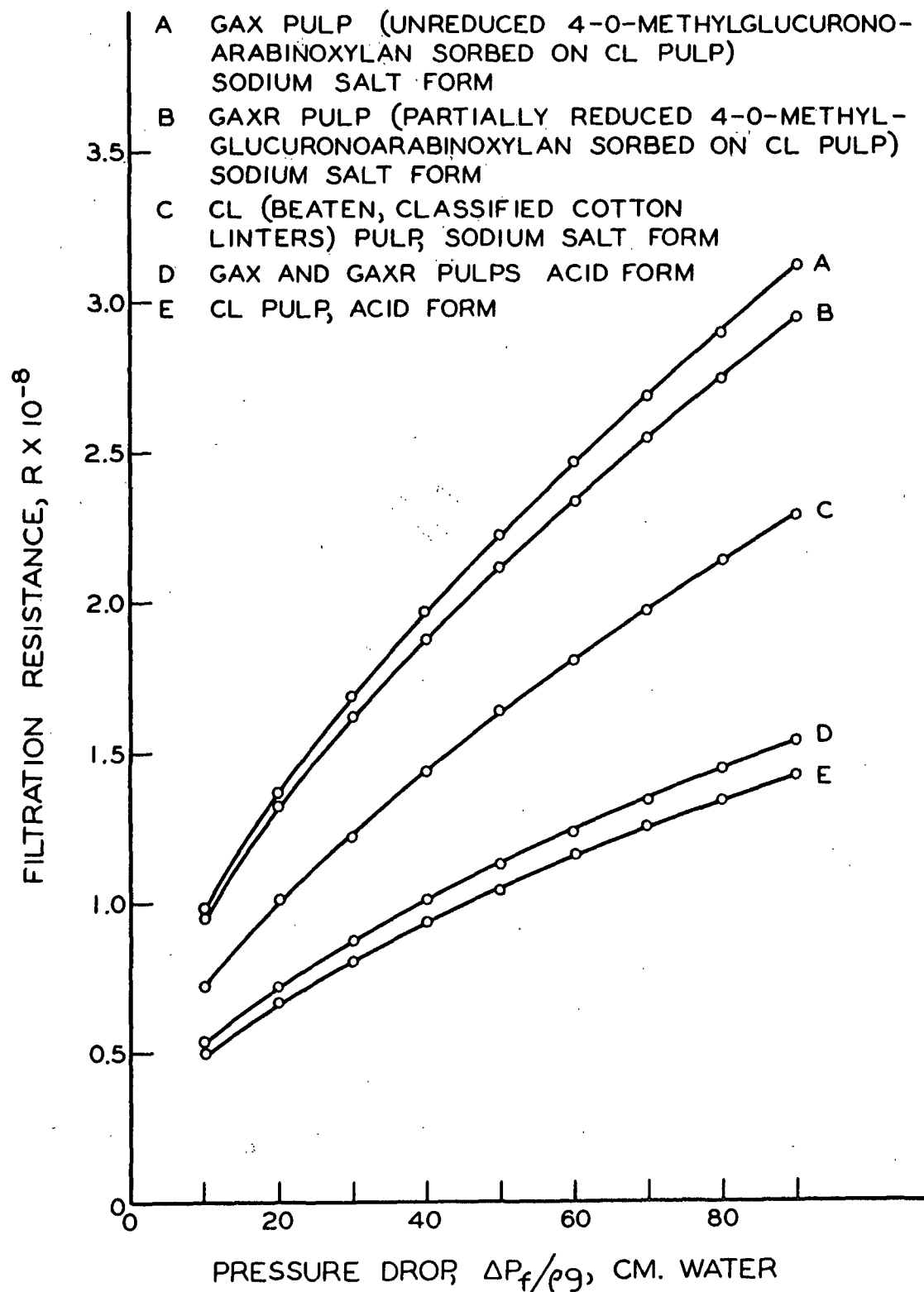


Figure 7. Filtration Resistance of Unbeaten Pulps

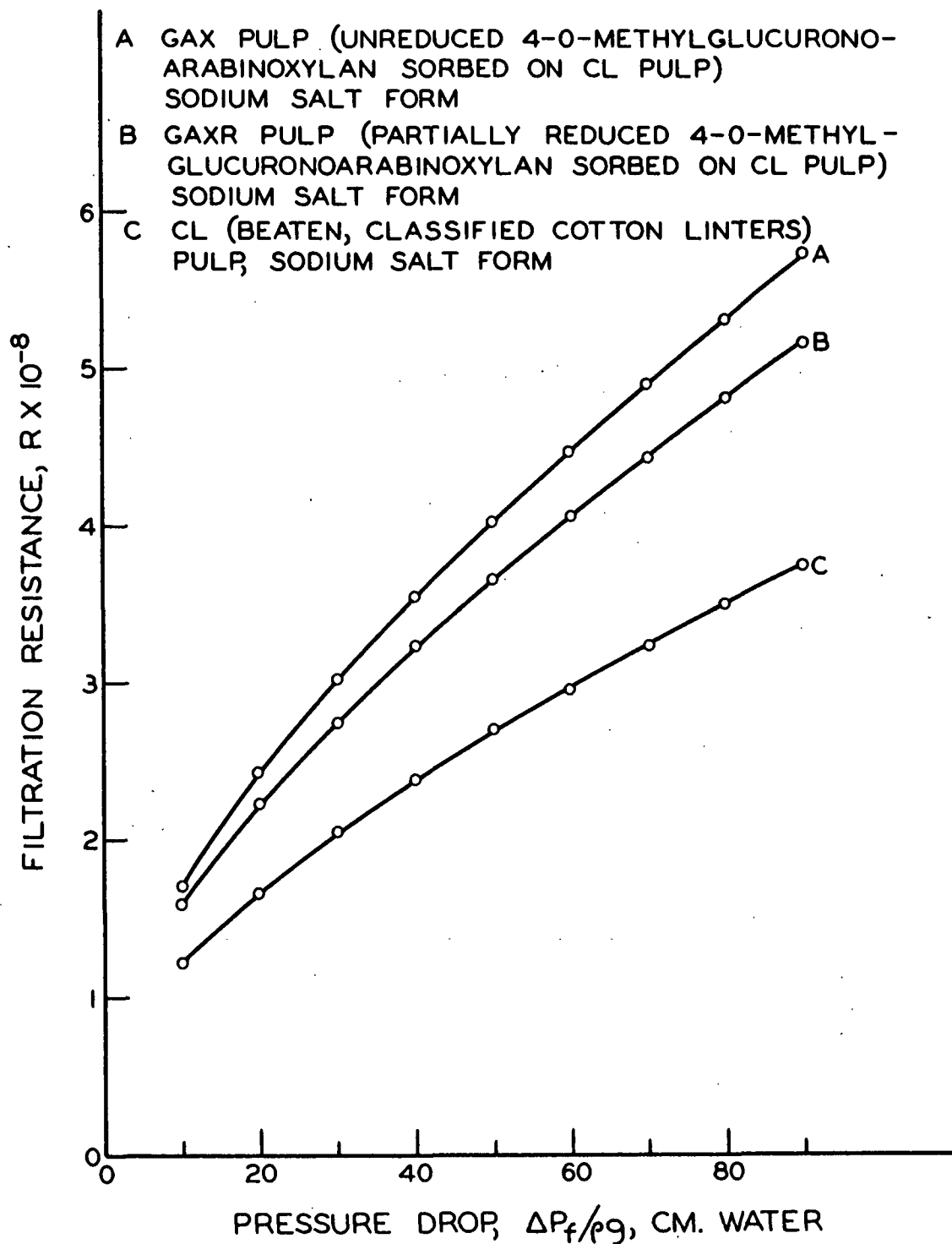


Figure 8. Filtration Resistance of Pulps Beaten
10 Minutes in Jokro Mill

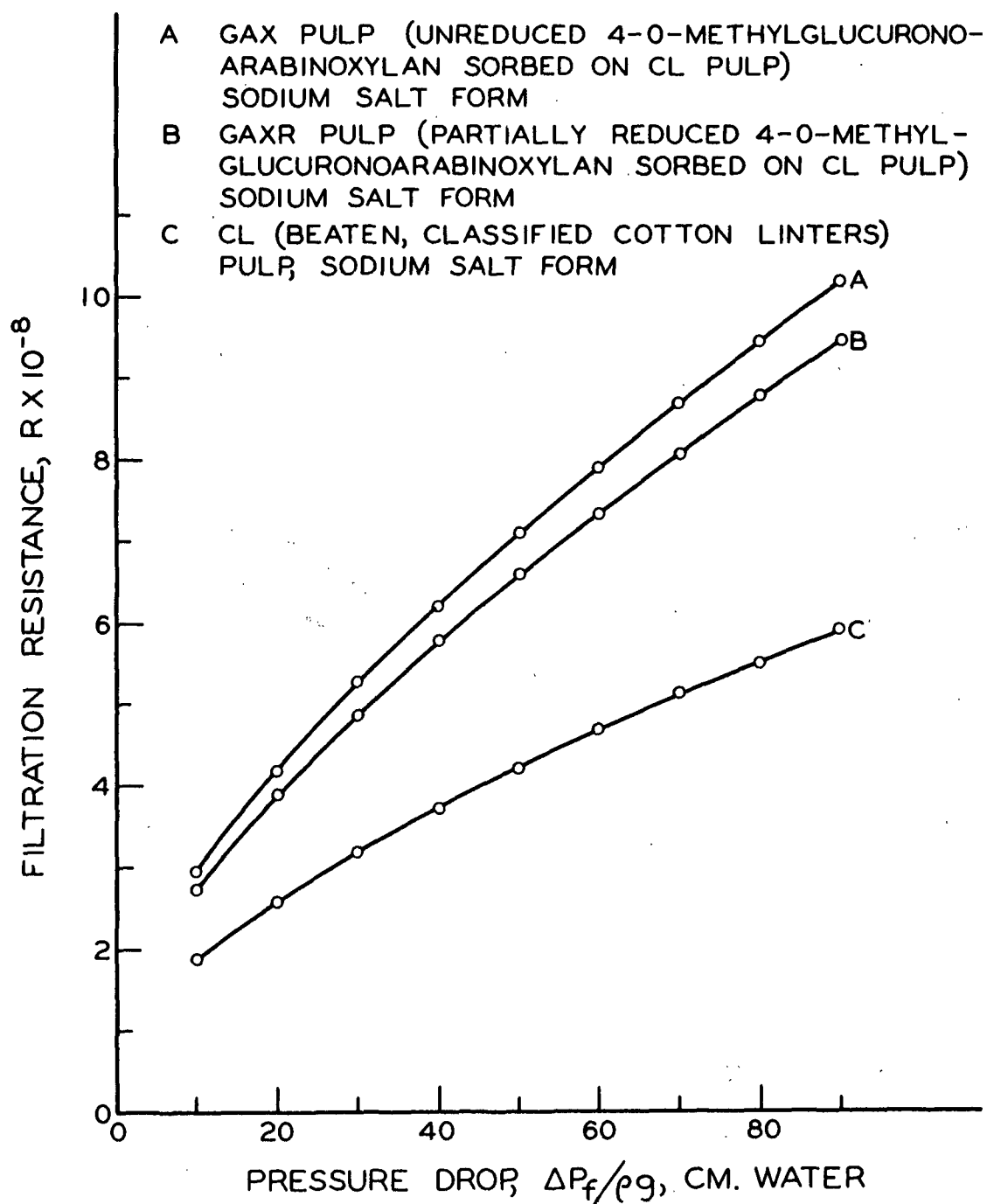


Figure 9. Filtration Resistance of Pulps Beaten
20 Minutes in Jokro Mill

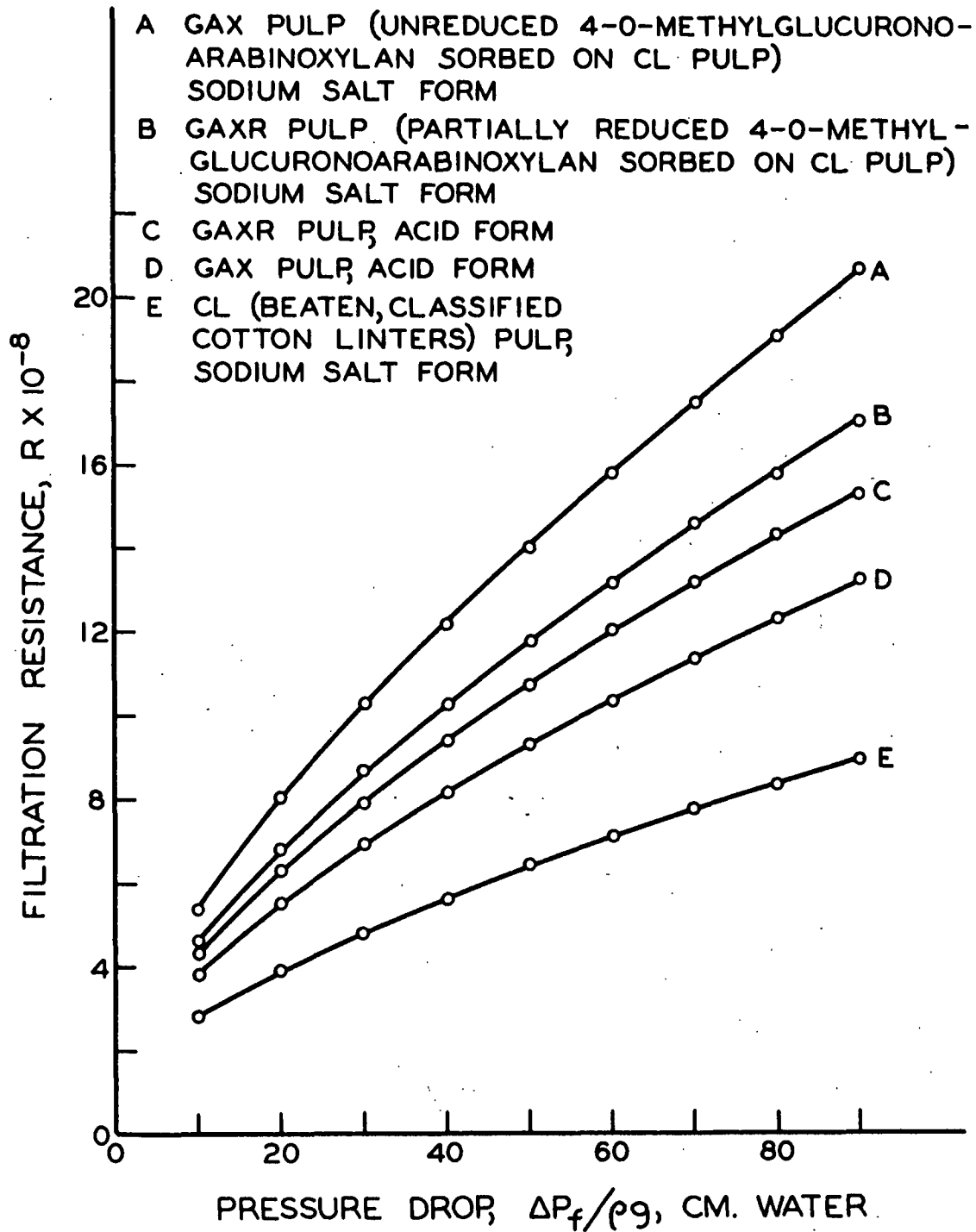


Figure 10. Filtration Resistance of Pulps Beaten 30 Minutes in Jokro Mill

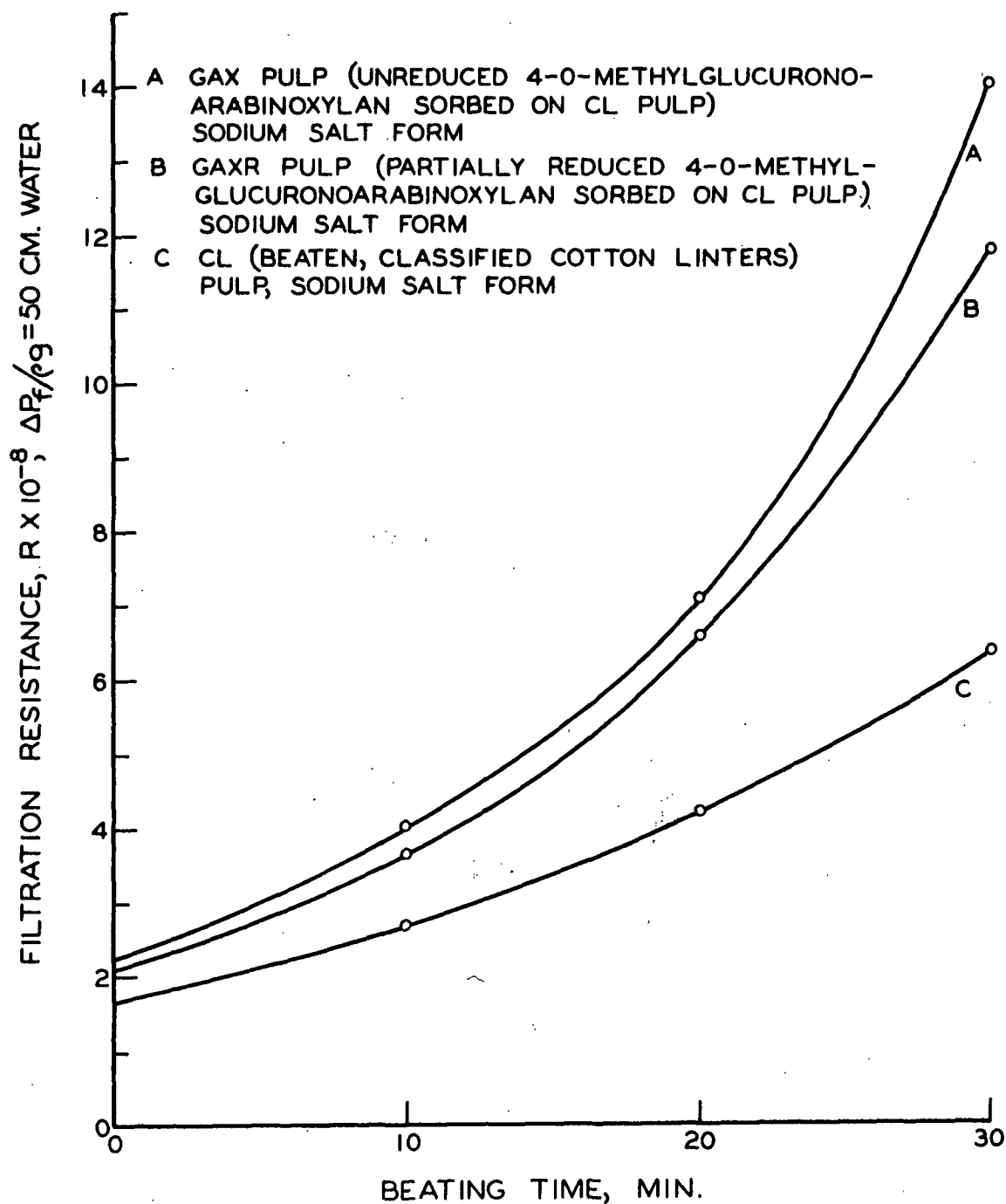


Figure 11. Filtration Resistance as a Function of Beating Time

identical with those given above with the exception that sodium bicarbonate was not added. These data are presented in Fig. 10. In this case there appears to be an anomalous behavior in the relative ranking of the GAX and GAXR pulps. The GAXR pulp has a greater filtration resistance than does the GAX pulp in the acid form. This difference may be explained by the polymer retention values after beating and filtration resistance determination shown in Table VI. With the exceptions of the acid form pulps at the 30-minute interval, the pulps lost only a small portion of the sorbed hemicellulose as a result of the beating action. The amounts lost by the GAX and GAXR pulps (sodium salt form) were very similar at each beating interval. In the acid media there should be less tendency for polymer desorption than in the slightly basic media. Yet the GAX pulp (acid form) polymer loss with beating was greater than that of the GAXR pulp (acid form). This loss could be a result of selfhydrolysis of the sorbed polymers in the free acid form.

TABLE VI
POLYMER RETENTIONS MEASURED AFTER BEATING AND
FILTRATION RESISTANCE DETERMINATION

Pulp	Form	Beating Interval, min.	Polymer Retention, mg./g.
GAX	salt	0	32.3
GAXR	"	0	32.5
GAX	"	10	30.1
GAXR	"	10	30.1
GAX	"	20	29.6
GAXR	"	20	30.5
GAX	"	30	29.1
GAXR	"	30	29.2
GAX	acid	30	27.5
GAXR	"	30	33.3

Specific surface and specific volume values were calculated from filtration and compressibility data. A comprehensive discussion of the factors involved in the technique of calculating surface area and volume values from filtration data is found in the papers by Ingmanson and co-workers (36-38). These workers have shown in the more recent publication (38) that the equation describing the filtration of a fibrous material should be written as follows:

$$\Delta P_f / \theta c^{1/2} = m + m n c^3 \quad (5)$$

$$\text{where } m = 3.5(1-N/2)v^{3/2} S_v^2 / B \quad (6)$$

$$n = 57 [(1-N/2)^2 v]^3 \quad (7)$$

$$c = M \Delta P_s^N \quad (8)$$

ΔP_f is the pressure drop across the fibrous mat, θ is filtration time, and c is the mat solids concentration. ΔP_s is the compacting pressure used in compressibility measurements, v is the specific fiber volume, and S_v is the specific fiber surface defined as the external area per unit volume of particles and is equal to S_w/v where S_w is defined as area per unit mass of particles. B is a constant for a given constant-rate filtration as previously discussed.

Values of ΔP_f , θ , and B may be determined in a constant-rate filtration of a fiber suspension, and compressibility measurements can be used to obtain values of the mat solids concentration, c , at compacting pressures equal to the pressure drops at which ΔP_f and θ were determined. Compressibility measurements are made on separate pulp samples (approximately 5 g.). The pulp slurry is added to the filtration tube and a pad is formed by the gradual downward motion of a permeable piston. Weights are added successively to the piston to compress the pad over a compacting pressure range of 8 to 147 cm. water. Pad thicknesses are measured

with a dialmicrometer. Due to the viscoelastic properties of a fibrous mat, thicknesses have to be measured at some arbitrary time. The values of \underline{N} are determined by measuring the slope of a plot of the logarithm of \underline{c} as a function of the logarithm of compacting pressure. Then from a plot of the left side of Equation (5) against \underline{c}^3 the value of the slope and the $\underline{c} = 0$ intercept are used to evaluate the specific surface, \underline{S}_w , and the specific volume, \underline{v} . These values are presented in Table VII.

TABLE VII
SPECIFIC SURFACE AND SPECIFIC VOLUME

Pulp	Form	Beating Time, min.	\underline{v} , cc./g.	\underline{S}_w , sq. cm./g.
GAX	salt	0	2.24	14,300
GAXR	"	0	2.19	14,100
CL	"	0	2.35	13,000
GAX	acid	0	2.13	10,700
GAXR	"	0	2.15	10,500
CL	"	0	2.19	10,400
GAX	salt	10	2.05	18,600
GAXR	"	10	2.01	18,100
CL	"	10	2.01	15,900
GAX	salt	20	2.09	23,600
GAXR	"	20	2.01	22,500
CL	"	20	2.04	19,700
GAX	salt	30	2.26	30,400
GAXR	"	30	2.04	29,100
GAXR	acid	30	2.06	29,500
GAX	"	30	2.03	27,200
CL	salt	30	2.06	23,000

The relative ranking of the GAX, GAXR, and CL pulps according to specific surface is consistent with the ranking of these pulps observed with filtration resistance. The remarkable difference in filtration resistance of the acid and

salt forms in Fig. 7 is also reflected in the specific surface values. The values of specific volume are somewhat random indicating that the specific volume was not changed enough to be detected by the filtration technique.

It was observed that the compressibilities of the GAX and GAXR pulps were greater than those of the corresponding control pulps. This observation was found consistently throughout the compressibility data presented in Table VIII. In terms of the quantity actually measured, this means that for a given weight of fibers and a given compacting pressure, the pulps containing sorbed hemicelluloses will compact to a greater extent than the control pulps. There appears to be a tendency toward increased compressibility with increasing beating for all three pulps.

HANDSHEET PROPERTIES

HANDSHEET PREPARATION

The GAX, GAXR, and cotton linters pulps (sodium salt form) at zero and 30-minute beating times were chosen for the evaluation of handsheet properties. It was expected from the filtration data that the zero beating time would produce handsheets of low strength and that differences between properties of the three pulps would be small. However, at zero beating time any difference in handsheet properties can be attributed directly to the physical presence of the sorbed hemicellulose and its uronic acid carboxyls. When the pulps are beaten, the resulting handsheet properties are a result of the physical presence of the hemicellulose polymers and the effects the hemicellulose polymers have on the beating action.

PULP COMPRESSIBILITY DATA

Pulp		Beating Interval	$\Delta P, \text{H}_2\text{O} \rightarrow \text{cm. H}_2\text{O}$	Mat. Solids Concentration, g./cc.					
Name	Form			<u>13.0</u>	<u>23.0</u>	<u>38.0</u>	<u>63.0</u>	<u>97.6</u>	<u>147.5</u>
CL	salt	0	0.061	0.075	0.094	0.115	0.138	0.164	0.193
"	"	0	0.064	0.077	0.095	0.116	0.140	0.166	0.192
"	"	0	0.065	0.077	0.097	0.118	0.141	0.165	0.194
	Average		<u>0.063</u>	<u>0.077</u>	<u>0.096</u>	<u>0.117</u>	<u>0.140</u>	<u>0.165</u>	<u>0.193</u>
CL	acid	0	0.064	0.078	0.096	0.117	0.139	0.165	0.193
"	salt	10	0.071	0.087	0.109	0.131	0.158	0.184	0.214
"	"	20	0.070	0.087	0.110	0.133	0.160	0.188	0.217
"	"	30	0.079	0.094	0.116	0.138	0.165	0.191	0.217
GAX	salt	0	0.070	0.084	0.104	0.124	0.149	0.175	0.205
"	"	0	0.071	0.085	0.103	0.124	0.149	0.174	0.203
"	"	0	0.070	0.083	0.101	0.124	0.146	0.174	0.203
GAXR	"	0	0.072	0.085	0.104	0.126	0.150	0.176	0.206
"	"	0	0.070	0.084	0.102	0.123	0.148	0.175	0.203
"	"	0	<u>0.072</u>	<u>0.085</u>	<u>0.104</u>	<u>0.124</u>	<u>0.149</u>	<u>0.172</u>	<u>0.203</u>
	Average		<u>0.071</u>	<u>0.084</u>	<u>0.103</u>	<u>0.124</u>	<u>0.149</u>	<u>0.174</u>	<u>0.204</u>
GAX	acid	0	0.068	0.080	0.098	0.114	0.142	0.169	0.199
GAXR	"	0	0.069	0.082	0.101	0.121	0.144	0.169	0.199
GAX	salt	10	0.074	0.091	0.114	0.137	0.165	0.194	0.225
GAXR	"	10	0.073	0.089	0.112	0.136	0.165	0.194	0.222
GAX	salt	20	0.081	0.097	0.119	0.143	0.164	0.196	0.231
GAXR	"	20	0.082	0.099	0.121	0.146	0.174	0.204	0.235
GAX	salt	30	0.088	0.104	0.125	0.149	0.167	0.197	0.228
GAXR	"	30	0.087	0.103	0.125	0.150	0.178	0.206	0.237
GAX	acid	30	0.081	0.097	0.119	0.141	0.170	0.200	0.231
GAXR	"	30	0.078	0.095	0.118	0.142	0.170	0.199	0.231

The 30-minute interval pulps were beaten in the Jokro mill as previously described. The zero beating time pulps were titrated to pH 8.0 with sodium bicarbonate and dispersed in the standard disintegrator for 300 counts. De-ionized water with a specific resistance of about 1.5 megohm-cm. was used in all subsequent dilutions and in filling the sheet mold. Handsheets were prepared under standard conditions (Institute Method 411).

RELATIVE BONDED AREA

The percentage bonded areas of the GAX, GAXR, and cotton linters pulps were determined by the so-called optical method based on the work of Parsons (39). This technique is based on the supposition that the scattering coefficient is proportional to the exposed unbonded area of the sheet. The ratio between total surface area and the unbonded area in a normal sheet is assumed to be equal to the ratio between the scattering coefficient of the "unbonded" handsheet and the scattering coefficient of the normal bonded sheet. The unbonded sheet is formed in water and the water is displaced by acetone and then by butyl alcohol without disturbing sheet formation. The percentage bonded area is equal to $100(S_u - S_p)/S_u$, where S_u is the scattering coefficient of the unbonded sheet, and S_p is the scattering coefficient of the normal bonded sheet. Although the results obtained with this technique are known to be too high, the technique can be used when only an estimate of bonded area is sufficient to rank a series of pulps.

The acetone-butanol handsheets were made with the cotton linters pulp (sodium salt form) at zero and 30-minute beating times. The scattering coefficients for unbonded sheets of the GAX and GAXR pulps probably would have been greater than those for the untreated cotton linters pulp. This would have

resulted in an increase in the calculated values of bonded area but not in the relative ranking of the pulps. The normal handsheets were made from the GAX, GAXR, and CL pulps (sodium salt form) at zero and 30-minute beating times. A General Electric recording spectrophotometer was used for measuring reflectance and transmission. From reflectance and transmission values the scattering coefficient is determined by reference to the Kubelka-Munk calculation charts and is converted to the specific scattering coefficient by dividing by the basis weight expressed in grams per square centimeter. The results are presented in Table IX.

TABLE IX
RELATIVE BONDED AREA OF HANDSHEETS

Pulp	Beating Time, min.	Specific Scattering Coefficient, sq.cm./g.	Relative Bonded Area, %
GAX	0	289	51.3
GAXR	0	305	48.6
Cotton linters	0	311	47.6
Unbonded sheets	0	593	--
GAX	30	294	71.4
GAXR	30	307	70.0
Cotton linters	30	384	62.4
Unbonded sheets	30	1022	--

STRENGTH PROPERTIES

The various strength tests were performed according to standard procedures. Tensile strength was measured using one-inch wide strips on the Instron instrument with a four-inch span. The results are presented in Table X. The viscosity-velocity product (VVP) for the zero beating time sheets was determined without a

TABLE X
HANDSHEET STRENGTH PROPERTIES

Pulp	GAX	GAXR	Cotton Linters
Zero Beating Time			
Basis weight, g./sq. m.	60.4	60.0	59.8
Formation	29.5	28.9	21.8
Caliper, 1/1000 inch	5.0	5.0	5.2
Apparent density, basis wt./caliper	12.1	12.0	11.5
VVP, kp. cm./sec.	67.7	65.4	38.8
Tear, g.	71	71	63
Instron tensile, lb.	8.0	7.6	5.7
Stretch, %	2.43	2.17	1.39
Tensile energy absorption, in.lb./sq.in.	0.14	0.12	0.06
30-Minute Beating Time			
Basis weight, g./sq. m.	61.3	61.2	62.7
Formation	55.2	54.1	51.9
Caliper, 1/1000 inch	4.0	4.0	4.4
Apparent density, basis wt./caliper	15.5	15.3	14.3
VVP, kp. cm./sec.	--	6.86	3.10
Tear, g.	58	54	51
Instron tensile, lb.	16.2	15.5	10.5
Stretch, %	3.83	3.48	2.85
Tensile energy absorption, in.lb./sq.in.	0.47	0.42	0.23

prefilm on the test strip due to the low range of values for these handsheets. The VVP values obtained for the GAX pulp at the 30-minute interval were not reported due to variability in this particular test result. The other strength tests had very good reproducibility. Directionality of stresses, detectable by VVP but not other properties, is believed to have been introduced into the GAX handsheets. z-Directional stresses could have been introduced across the sheet in the direction of couching.

Strength test results in Table X generally reflect the rankings obtained from the filtration data. The pulps containing the sorbed hemicelluloses have considerably better strength properties than the cotton linters control pulp. The pulps containing the unreduced polymer, GAX, have better properties than the pulps containing the reduced polymer. These differences are small, but they are significant.

DISCUSSION OF RESULTS

POLYMER PREPARATION AND CHARACTERIZATION

The hemicellulose polymer, 4-O-methylglucuronocarabinoxylan (GAX), was selected for this study because: 1) the polymer had been previously isolated and examined, and 2) the polymer is very soluble in water and in acidic media. The second reason proved to be very important in the sorption studies. The polymer source, an alkaline sulfite (sulfide) spruce pulp, was selected rather than a holocellulose because it was known that GAX could easily be isolated from this pulp in quantity.

The design of this study required that there should be little or no difference in the molecular properties of the reduced and unreduced polymers. Therefore, the unreduced polymer was subjected to full acetylation and deacetylation so that the reduced and unreduced polymers would be subjected to comparable conditions except for the reduction step. McKee (18) reported an increase in intrinsic viscosity of his polymer after acetylation, reduction, and deacetylation as found in this study. He concluded that a portion of the lower molecular weight material had been lost. The intrinsic viscosities of the reduced and unreduced polymers prepared in this study are very similar, but both are greater than the intrinsic viscosity of the polymer as isolated from the pulp. This indicates that acetylation and deacetylation of the unreduced polymer was a desirable procedure.

The gaseous diborane reduction technique in contrast to the conventional, was used successfully for the reduction of uronic acid carboxyls without the production of the by-product. The preliminary experiments indicated that the presence of boron trifluoride etherate in the reaction flask is essential in

producing the by-product. The possible utility of the gaseous diborane technique was suggested by the fact that Ross (25) found no by-product in the hydrolyzate of a neutral trisaccharide McKee (18) prepared from aldotriouronic acid by gaseous diborane. Carbon dioxide data and chromatographic analysis indicate that reduction in the present case caused no apparent changes in the polymer other than reduction of the uronic acid carboxyls.

The degree of reduction achieved (60%) is probably related to carboxyl accessibility because the solvent produced a colloidal dispersion and not a true solution. An increased reduction should be achieved if the partially reduced acetate is precipitated and subjected to reduction several times. A reduction greater than that achieved was not desirable in this study since a further decrease in polymer solubility could have resulted.

This study demonstrates that reduction of the uronic acid carboxyls can significantly lower the solubility of a hemicellulose polymer in water. The physical presence of side-branches of arabinose and 4-O-methylglucuronic units were believed to contribute to the solubility of this particular polymer. This contribution presumably is of far less importance than that of the uronic acid carboxyls.

The actual location of these branching units along a linear xylan chain are misrepresented by the procedure of reporting sugar ratios. These ratios only indicate that on the average there are a given number of side-branches for a given number of monomers in the linear chain. The ratio offers no proof that a given unit is repeated regularly. The polymer used in this study has a sugar ratio of 8:1:1 (xylose:arabinose:4-O-methylglucuronic acid). Methoxyl data

from the GAX acetate fractionation indicates that the side-branches of 4-O-methylglucuronic acid are not repeated regularly along the xylan chain.

The GAX acetate fractionation data and measured $\frac{M_w}{M_n}$ ratio indicate this polymer has a very narrow molecular weight distribution. These data with the number average molecular weights and intrinsic viscosities of the reduced and unreduced polymers suggest that these polymers are very similar in molecular weight and distribution. This minimizes the possibility of molecular differences affecting relative sorption of the reduced and unreduced polymers.

SORPTION STUDIES

Sorption studies with the reduced and unreduced polymers permitted a further insight into the mechanisms involved in the sorption of hemicellulosic beater adhesives on cellulose pulps. A very significant contribution was the discovery that the uronic acid carboxyls of a hemicellulose polymer can greatly reduce sorption of the polymer from water solution by a cellulose substrate (Table III). This result requires a more careful interpretation of Most's (7) work with four slash pine hemicellulose fractions. These fractions had an increasing mannan content and a decreasing uronic acid content. In fact, the uronic acid content of the first fraction was more than twice that of the fourth fraction. The retention of the fourth fraction on a bleached sulfite pulp was nearly three times that of the first fraction. Most stated, "The hemicelluloses having the higher mannan content also had the higher sorption rates." However, he carefully avoided a direct statement that increased mannan content was the only reason for increased retention. Most's work has been considered proof that the difference in chemical composition of a mannan and a xylan (predominantly the presence of a sixth carbon atom with a primary hydroxyl in the former case) is

the reason the fractions of higher mannan content were better beater adhesives. Certainly this chemical difference must have an effect, but the effect is presumably subordinate to the decreased polymer solubility of polymer species of lower uronic acid contents in hemicellulose mixtures as an explanation for increased polymer retention.

Although adsorption generally increases with decreasing solubility, there are many exceptions to the rule. In the particular case of hemicellulose sorption, the validity of the rule had not been determined prior to this study. In the range of natural uronic acid carboxyl contents, the solubility and subsequently the sorbability of hemicellulose polymers are a function of uronic acid carboxyl content. However, this statement should not be extrapolated to synthetic polymers of very high carboxyl content.

Schmorak and Adams (40) prepared a series of carboxymethylated 4-O-methyl-glucuronoxylans with a D.S. range of about 0.15 to 0.92. A fully substituted xylan polymer would have a D.S. of 2. The adsorption of these carboxymethylated polymers by cotton linters was measured in experiments which were not carefully controlled. The techniques used to measure retention were not very sensitive and adsorption was not detected until the higher D.S. samples were used. This indicated that sorption increased with increasing carboxyl content at higher D.S. The carboxyl-carboxyl hydrogen bond energy of formation (exothermic) is greater than that of a hydroxyl-hydroxyl bond (41, 42). Thus, the carboxyl-carboxyl bond would be thermodynamically preferred. Perhaps the effect of solubility is overcome when a sufficient number of carboxyls are present and sorbability increases with further increase in carboxyl content.

This study showed that comparable retentions of two hemicellulose polymers containing different carboxyl contents could be achieved in the presence of an electrolyte such as hydrochloric acid. In fact, the magnitude of retention was increased several orders for both the reduced and the unreduced polymer. The presence of hydrochloric acid evidently created a poorer solvent for the polymers; however, there was no visual indication of precipitation when hydrochloric acid was added to water solutions of the two polymers. Low concentrations of simple electrolytes are often used in viscometry to suppress ionization of polyelectrolytes in solution. The observed "polyelectrolyte effect" in viscometry, the anomalous increase in reduced viscosity of a polyelectrolyte polymer solution as concentration decreases, is attributed to the presence of charged groups (e.g., ionized carboxyl) along the polymer chains. With more concentrated solutions, the effect of these charges appears to be masked by the presence of other polymer chains. However, as the polymer concentration decreases, the mutually repulsive forces of the charges along the chains become more marked and the polymer chains tend to assume extended configurations. An extended molecule contributes more to the viscosity of the solution than does a coiled molecule and the result is an increase in the reduced specific viscosity as the polyelectrolyte concentration decreases. The addition of simple electrolytes reduces the amount of charged groups along the polymer chains by suppressing ionization and this permits the polymers to assume smaller volumes even at low polymer concentration.

The acidic sorption solution (0.02N HCl) apparently did not have any adverse effect on the intrinsic viscosity (Table IV) of the polymers subjected to the solution without pulp (48 hr., 30°C.). Equal retentions of these two polymers may have been accomplished by selection of different sorption conditions, e.g., pulp and polymer concentrations, for each of the polymers. However, electrolyte

addition was chosen instead because this has the additional advantage of suppressing any polyelectrolyte behavior of these polymers. The different carboxyl contents could produce a difference in the polyelectrolyte behavior of the reduced and unreduced polymers, resulting in different molecular configurations of the polymers in water solution and thus a difference in the configurations of the sorbed molecules.

Even extensive beating removed only a small portion of the sorbed hemicelluloses thus indicating that the polymers are tenaciously sorbed by the cellulose substrate. This suggests that the polymers are sorbed with a large number of their segments in direct contact with the surface. Silberberg (20) believes that the fraction which these segments constitute of the polymer molecule is of order 0.5; whereas, in earlier publications on theoretical considerations of polymer adsorption, Frisch, Simha, and Eirich (43, 44) predicted that only a few segments of a flexible macromolecule would be adsorbed. Presumably, the driving force in sorption is related to the thermodynamics of the solute-solvent-substrate system and it would seem logical to suppose that among different systems there could be a wide range of values for the fraction of segments sorbed. For a given solute and substrate, the fraction of segments sorbed would be expected to increase when poorer solvents are used because the total change in free energy would increase as the difference between the change in free energy due to desolvation of the polymer where adsorption occurs (and the corresponding sites on the substrate in some cases) increases. Silberberg (20) proposed that there can be stretches of segments all in contact with the surface alternating with non-contacting loops of random numbers of segments. In the case of polyelectrolyte adsorption, the loops are predicted to be long. It seems logical to assume that long loops would be more susceptible to cleavage by the mechanical action of

beating. Upon cleavage, a large portion of these long loops would be dissolved in the supernatant liquid. This would result in a significantly lower sorbed polymer content.

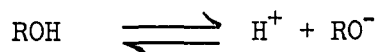
The lower intrinsic viscosity values (Table IV) for the polymers recovered from the supernatant solvent after sorption indicates that molecules of higher molecular weight were preferentially sorbed. However, similar molecular weight species of the unreduced and reduced polymers were sorbed in the preparation of GAX and GAXR pulps, respectively. This effect is probably related to differences in the solubilities of the species of higher and lower molecular weight. The fact that polymer solubility generally decreases with increasing molecular weight is well known and is used to fractionate polymer solutions into fractions of graded molecular weight. Preferential sorption in other polymer-substrate-solvent systems is known and has been used to fractionate polymer samples where molecular weights were not too high (20). Factors other than the correlation between polymer solubility and molecular weight can cause preferential sorption of species of a particular molecular weight, e.g., Swenson (45) hypothesized that apparent preferential sorption of lower weight cellulose acetate molecules with porous charcoal (acetone solvent) was due apparently to preferential diffusion of lower weight molecules onto porous charcoal.

The methylene blue adsorption data and the methoxyl contents of the supernatant polymer GAXS indicate that in the presence of 0.02N hydrochloric acid there was little or no preferential sorption of fractions of lower or higher carboxyl content.

FILTRATION RESISTANCE

The filtration data (Fig. 7-11) confirm the hypothesis that the uronic acid carboxyls of 4-O-methylglucuronarabinoxylan can affect the hydrodynamic properties of the cellulose pulp on which the hemicellulose polymer is sorbed. The ionic nature of the uronic acid carboxyls in the sorbed hemicelluloses proved to be important in measuring filtration resistances of the GAX and GAXR pulps. The more hydrophilic salt form increased filtration resistance significantly. The very different behaviors of the sodium salt and acid forms of the hemicellulosic carboxyls in this study are consistent with the differences Talwar (14) reported for the salt and acid forms of low D.S. CMC pulps.

The preparation of the salt form was accomplished by titration of the pulps to pH 8.0 with sodium bicarbonate. This weakly alkaline titration also increased the filtration resistance of the cotton linters control pulp. This could be anticipated because the control pulp contains some carboxyls and an increase in solvent basicity would increase the solvation of free hydroxyls. According to the Lewis definition, an aliphatic hydroxyl group may be considered an acid in the same manner in which a carboxyl is acidic as indicated by



The acidity constant of an acid is directly proportional to the basicity of the solvent. Thus, as the basicity of the solvent increases, the equilibria indicated above would shift to the right causing an increase in ionization and hydration. Certainly the acidity of an individual hydroxyl would be many times less than the acidity of a carboxyl. However, hydroxyl acidity can be significant with a material such as cellulose which contains a very large number of hydroxyls.

It is evident that the presence of the hemicellulosic beater adhesive was detectable by the surface areas measured with the filtration technique. It is believed that this observed result was due not only to the physical presence of the sorbed hemicelluloses but also to an increase in the hydrophilic nature of the fibrils containing the sorbed beater adhesives. This increase in the fibrils' affinity for water caused the fibrils to be more extended from the fiber surface into the surrounding solution, thus increasing the amount of exposed fiber surface. This effect would be expected to improve fiber association and interfiber bonding on a molecular scale.

The difference between the filtration resistances (Fig. 11, and surface areas, Table VII) of the GAX and GAXR pulps (sodium salt form) increased from small values at zero beating time to large values after a 30-minute beating period. This demonstrates that the response of pulps to beating, as measured by filtration resistance, can be affected by the presence of uronic acid salts in sorbed hemicelluloses. These hemicellulosic uronic acid salts are important because they increase the hemicellulose's affinity for water.

In water solution, a hydrophilic material such as the hemicellulose polymer used in this study would be hydrated and should have a larger "effective volume" than would be anticipated from an observation of its physical volume. However, specific fiber volume as measured by the filtration technique did not appear to be affected by the presence of the sorbed hemicellulose. This indicates that either water of hydration is not detected by the filtration technique or that the contribution of the sorbed hemicellulose to swollen fiber volume in this study was too small to be detected within the accuracy of the technique used. Ingmanson (46) believes the accuracy of specific volume measurement with the filtration

technique is of the order of 10%. Since the sorbed hemicelluloses are present to the extent of about 3.5%, their swollen volume detectable by filtration must be less than three times their dry volume.

The early observation that the compressibility of a given pulp remains practically unchanged over a wide range of mechanical beating was not anticipated since compressibility was believed to be a direct measure of fiber flexibility and beating was believed to result in a more flexible fiber. However, Jones (47) concluded that compressibility measurements cannot be used as general test for fiber flexibility and that the complications introduced by differences in fiber length-to-diameter ratio make it unwise to compare pulps from different species of wood, different fractions of the same pulp or samples of the same pulp at different degrees of refining. Jones considered three predominant mechanisms in the compression of a fibrous mat: fiber bending, fiber slippage, and fiber deformation. The importance of the fiber's elastic modulus is evident in fiber bending and fiber deformation.

It is uncertain whether or not the hemicellulose polymers sorbed on the cellulose fibers in this study changed the elastic modulus of the fibers, because the hemicellulose polymer sorption sites were not located throughout the structure of the fiber. The major portion of the sorbed polymers was probably located in the fibrillated structure of the external fiber surface. Sorption may have occurred also in the lumen surfaces when fibers were cut or broken and the lumen was exposed. The sorbed hemicelluloses constituted a large percentage of a fiber's external fibrillated structure. Thus, the elastic modulus of the fibrils could have been affected and could have increased fiber deformation at points of contact. However, the sorbed hemicellulose's greatest contribution to increased compressibility was probably through the mechanism of fiber slippage. The

presence of a hydrophilic material over most of a fiber's external surface would be expected to cause a "lubrication effect" resulting in an increase in the ability of two fibers to slip past each other under the influence of a compacting pressure in a water suspension.

Talwar (14) found that while CMC pulps in the sodium salt form show vastly increased specific volumes and compressibility, the acid form showed no such changes over those shown by the control pulps. Furthermore, the compressibility of these CMC pulps increased with increasing degree of carboxymethylation. Since the compressibility values varied appreciably with pH, Talwar could not believe that fiber flexibility was involved in this very reversible and instantaneous behavior. However, he did not consider the fact that the sodium salt form of his CMC pulps is more hydrophilic than the acid form and that this difference in hydrophilic nature could affect the elastic modulus of the CMC fibers and inter-fiber slippage in a fibrous mat. It should be emphasized that through the technique of substitution Talwar's CMC fibers contained carboxymethyl groups not only on the surfaces but throughout the fibers.

HANDSHEET PROPERTIES

The handsheet data (Tables IX and X) are consistent with the results anticipated on the basis of the generally accepted concept of the importance of the hydrophilic nature of fibers to fiber bonding and resulting sheet strength. Leech (48) suggested that the strength of paper depends upon four factors; the strength of fibers, the strength of fiber-to-fiber bonds, the number of bonds (bonded area), and the distribution of bonds as indicated by the fiber distribution or sheet formation. He concluded that beater adhesives contribute to the strength of paper by affecting one or more of these factors and showed that with

locust bean gum the contribution of each factor was as follows: increased fiber strength, 0%, increased bonding strength, 60%, increased bonded area, 15%, and improved formation, 25%.

It is apparent from Table X that the uronic acid carboxyls (sodium salt form) contribute to the influence hemicellulosic beater adhesives have on paper strength properties. The observed magnitude of carboxyl contribution was not as great as that due to the hemicellulose polymer, per se. However, the contribution is quite large when the small difference in carboxyl contents of the GAX and GAXR pulps is considered.

Tensile values indicate the presence of hemicelluloses and uronic acid carboxyls increased over-all fiber bonding. Relative bonded area values indicate an increase in the number of bonds. Formation and, in particular, tensile energy absorption values suggest improvement in bond distribution.

Swanson (49) reported that the addition of locust bean and guar gums to a beaten sulfite pulp caused large increases in tensile strength and decreases in tear strength. However, tear values for a given beating interval in the present study increased with increasing tensile. Perhaps the decrease in sheet density was insufficient to offset the contribution which improved bond distribution made to tearing strength.

This study confirms Talwar's conclusion that the observed strength improvement in paper made from low-substituted carboxymethyl pulps can be attributed to the hydrophilic nature of the carboxyl groups (sodium salt form). The method Talwar employed to introduce carboxyl groups into pulp was very different from the technique used in this study. Talwar introduced carboxymethyl groups into

the pulp by chemical reaction and the size of the substituted group and the nature of the reaction conditions probably caused substitution within the fiber structure as well as on the fiber surface. Whereas, in the present study carboxyl groups were introduced into pulps through the sorption of a hemicellulose polymer containing uronic acids. Obviously, the size and configuration of the groups accompanying the carboxyl are different in each of the above cases and the location of these groups in the fiber structure are different. However, these factors appear to be subordinate to the contribution of the carboxyl group, per se. The observed effects on fibrous properties were greater in Talwar's study probably because the carboxyl content of his pulps was several times greater than that of the pulps in this study.

CONCLUSIONS

A gaseous diborane reduction technique was used successfully for partial reduction of the uronic acid carboxyls of a 4-O-methylglucuronoarabinoxylan. This reduction significantly lowered the solubility of this polymer in water and the sorption of this polymer from water solution on a beaten, classified cotton linters pulp increased with decreasing carboxyl content. Addition of hydrochloric acid to the sorption mixture suppressed the ionization of the carboxyl groups and almost identical retentions of the reduced and unreduced polymers were achieved. The retentions observed in the presence of 0.02N hydrochloric acid were several orders of magnitude greater than those observed when water was used as the solvent during sorption. Preferential sorption of higher molecular weight polymer species on the cellulose substrate occurred with the material and conditions used in this study. However, there is no indication of preferential sorption of species of lower or higher carboxyl content in the presence of hydrochloric acid.

The presence of the sorbed hemicellulose and its uronic acid salts apparently increased the ability of the fibrillated fiber structure to interact with water and thereby increased the amount of accessible fibrillar area. This increase in accessible fibrillar area was realized by an increase in the filtration resistance of the pulps containing sorbed hemicellulose with the uronic acid carboxyls in the salt form, whereas much lower values were observed with these carboxyls in the acid form. Filtration resistance increased more rapidly with beating, and handsheet strength properties were improved when these uronic acid salts were present. The compressibility of the cellulose substrate was increased by the presence of the sorbed hemicellulose probably due to a "lubrication effect" which increased interfiber slippage.

ACKNOWLEDGMENTS

There are many persons who, through advice and assistance, contributed to this investigation and I am sincerely grateful to all these persons. In particular, I would like to thank H. A. Swenson for the GAX acetate fractions, H. A. Swenson and C. Schmitt for the osmometry and light-scattering data, R. Van Eperen for the handsheet VVP data, O. Kuehl for the actual operation of the filtration apparatus, and W. Shillcox for the handsheet reflectance and transmission data.

I am especially indebted to my thesis advisory committee, H. A. Swenson, J. W. Swanson, and N. S. Thompson, for the many hours of counsel through all the phases of this thesis.

LITERATURE CITED

1. Wise, L. E., Paper Ind. 37, no. 11:1024-6, 1062(Feb., 1956).
2. Swanson, J. W., Tappi 39, no. 5:257-70(May, 1956).
3. McKenzie, A. W., and Higgins, H. G., Svensk Papperstid. 61:893-901(1958).
4. Dickey, E. E., Tappi 43, no. 9:195-7A(Sept., 1960).
5. Thompson, N. S., Peckham, J. R., and Thode, E. F., Tappi 45, no. 6:433-42 (June, 1962).
6. Thompson, J. O., Swanson, J. W., and Wise, L. E., Tappi 36, no. 12:534-41 (Dec., 1953).
7. Most, D. S., Tappi 40, no. 9:705-12(Sept., 1957).
8. Swanson, J. W., Tappi 44, no. 1:142-81A(Jan., 1961).
9. Bletzinger, J. C., Ind. Eng. Chem. 35, no. 4:474-80(April, 1943).
10. Aiken, W. H., Ind. Eng. Chem. 35, no. 11:1206-10(Nov., 1943).
11. McKenzie, A. W., and Higgins, H. G., Australian J. Appl. Sci. 6, no. 2: 208-17(June, 1955).
12. Harrison, J. J., Paper Trade J. 119, no. 5:28-38(Aug. 3, 1944).
13. Walecka, J. A., Tappi 39, no. 7:458-63(July, 1956).
14. Talwar, K. K., Tappi 41, no. 5:207-15(May, 1958).
15. Wurz, O., and Swoboda, O., Papier-Fabr. 37, Tech. Tl.:125-7(1939); C.A. 33:5653.
16. Jayme, G., and von Köppen, A., Papier 4, no. 19/20:373-8; no. 21/22:415-20; no. 23/24:455-62(Oct.-Dec., 1950); C.A. 45:3594.
17. Saarnio, J., Paper and Timber (Finland) 35:217-19(1953).
18. McKee, S. C. An investigation of the hydrolysis of a reduced 4-O-methyl-glucuronoxylan. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1961. 53 p.; McKee, S. C., and Dickey, E. E., J. Org. Chem. 28:1561-3(1963).
19. Bikerman, J. J. Surface chemistry, theory and applications. 2d ed. p. 293. New York, Academic Press, 1958.
20. Silberberg, A., J. Phys. Chem. 66:1872-1907(1962).

21. Peckham, J. R., and Van Drunen, V., Tappi 44, no. 5:374-84(1961).
22. Carson, J. F., and MacLay, W. D., J. Am. Chem. Soc. 70:293-5(1948).
23. Genung, L. B., and Mallatt, R. C., Ind. Eng. Chem. Anal. Ed. 13:369-74(1941).
24. Thompson, N. S. Personal communication, 1962.
25. Ross, R. Personal communication, 1963.
26. Brown, H. C., and Subba Rao, B. C., J. Am. Chem. Soc. 82:681-6(1960).
27. Brown, H. C., and Tierney, P. A., J. Am. Chem. Soc. 80:1552-8(1958).
28. Yundt, A. P. The preparation, characterization, and hydrolysis of crystalline and amorphous xylan. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1949. 200 p.
29. Swenson, H. A., and Schmitt, C. Unpublished work, 1963.
30. Flory, P. J. Principles of polymer chemistry. Ithaca, N. Y., Cornell University Press, 1953. 672 p.
31. LaBel, R. G., and Goring, D. A., J. Polymer Sci. part C, no. 2:29-48(1963).
32. Shriver, E. H., Tappi 38, no. 8:482-93(Aug., 1955).
33. Saeman, J. F., Moore, W. E., Mitchell, R. L., and Millet, M. A., Tappi 37:336(1954).
34. Davidson, G. F., J. Textile Inst. 39, no. 3:T65-86(March, 1948).
35. Wilson, W. K., and Mandel, J., Tappi 44, no. 2:131-7(Feb., 1961).
36. Ingmanson, W. L., and Whitney, R. P., Tappi 37, no. 11:523-34(Nov., 1954).
37. Whitney, R. P., Ingmanson, W. L., and Han, S. T., Tappi 38, no. 3:157-66 (March, 1955).
38. Ingmanson, W. L., and Andrews, B. D., Tappi 46, no. 3:150-5(March, 1963).
39. Parsons, S. R., Paper Trade J. 115, no. 25:34-42(Dec. 14, 1942).
40. Schmorak, J., and Adams, G. A., Tappi 40, no. 5:378-83(May, 1957).
41. Pimentel, G. C., and McClellan, A. L. The hydrogen bond. San Francisco, W. H. Freeman Co., 1960. 475 p.
42. Mark, H., and Tobolsky, A. V. High polymers II. Physical chemistry of high polymer systems. 2d. ed. p. 120-51. New York, Interscience Publishers, 1950.

43. Frisch, H. L., Simha, R., and Eirich, F. R., J. Chem. Phys. 21:365-6(1953).
44. Frisch, H. L., Simha, R., and Eirich, F. R., J. Chem. Phys. 57:584-9(1953).
45. Swenson, H. A., Acta Chem. Scand. 9, no. 4:572-82(1955).
46. Ingmanson, W. L. Personal communication, 1963.
47. Jones, R. L. An investigation of the effect of fiber structural properties on the compression response of fibrous beds. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1962. 158 p.; Tappi 46, no. 1:20-8(Jan., 1963).
48. Leech, H. J., Tappi 37, no. 8:343-9(Aug., 1954).
49. Swanson, J. W., Tappi 33, no. 9:451-62(Sept., 1950).
50. Leech, H. J., Tappi 37, no. 7:290-4(July, 1954).

APPENDIX I

GLOSSARY OF ABBREVIATED TERMS

- CL Pulp --- cotton linters pulp refined under standard conditions for 90 minutes in a Valley laboratory beater and processed through a Bauer-McNett classifier. The fraction passing the 150-mesh screen was discarded.
- GAX --- hemicellulose polymer, 4-O-methylglucuronoarabinoxylan, isolated from an alkaline sulfite (sulfide) spruce pulp by extraction with 5% NaOH. Further treatment consisted of full acetylation followed by deacetylation with 5% KOH.
- GAX Pulp -- CL pulp containing GAX sorbed under the following conditions:
2 g. pulp/100 g. solution, solution 0.02N HCl, 5% polymer based on pulp, constant temperature 30°C., and a sorption period of 48 hours.
- GAXR -- partially (60%) reduced GAX polymer prepared by passing gaseous diborane through a dispersion of the GAX acetate in tetrahydrofuran. The GAXR acetate was deacetylated with 5% KOH.
- GAXR Pulp-- CL pulp containing GAXR sorbed under conditions identical to those used to prepare the GAX pulp.
- GAXRS -- polymer isolated from the supernatant liquid after preparation of GAXR pulp.
- GAXS -- polymer isolated from the supernatant liquid after preparation of GAX pulp.
- TFE -- trifluoroethanol.

APPENDIX II

EXPERIMENTAL PROCEDURE

HEMICELLULOSE ISOLATION

PULPING PROCEDURE

The chip fraction passing the one-mesh screen and retained on the four-mesh screen was selected for pulping. The chips were pulped by an alkaline sulfite (sulfide) cook as outlined by Peckham and Van Drunen (21). Two cooks were made with the following conditions:

Wood -- weight/charge -- 4950 g. ovendry basis

moisture -- 15.7%

Liquor/wood ratio -- 4.7

Na_2SO_3 -- 2792 g. (6% solution as SO_2)

Na_2CO_3 -- 223 g. (4.5% on ovendry wood)

Na_2S -- 223 g. (4.5% on ovendry wood)

Time to maximum temperature (176°C.) -- 2 hr.

Time at maximum temperature -- 6.5 hr.

The pulps were slushed in the Sprout-Waldron refiner and screened with two Valley flat screens. The screenings (about 0.5% on ovendry wood) were dried, weighed, and discarded. The screened pulp was centrifuged (30% solids) and stored in polyethylene bags. The total yields of the two cooks were 44.3 and 43.8% based on the ovendry wood.

HEMICELLULOSE EXTRACTION

The two pulps were combined (about 3800 g.) and divided into five equal portions. Each portion was extracted with 5% sodium hydroxide (room temperature)

in a large Buchner funnel. A total of 19 liters of 5% sodium hydroxide was used. Portions of the caustic solution were recycled, intermittently removed and acidified to pH 5 with acetic acid. An additional 26 liters of 5% sodium hydroxide were added to the pulp residue, intermittently stirred in a stainless steel tank for one hour, and removed by filtration. This extract was acidified (pH 5) and added to the initial extract for a total volume of 41 liters.

The acidified extract was filtered through a coarse fritted glass funnel and concentrated under vacuum to 15 liters in a large laboratory evaporator. Two volumes of 95% ethyl alcohol were added and the precipitated hemicelluloses were removed by filtration.

The light tan precipitate was dissolved in 5 liters of distilled water and bleached with sodium chlorite (120 g. NaClO_2 over a 4-hour period, pH 5, 35-45°C.). The reaction mixture was filtered and two volumes of 95% ethyl alcohol were added. The precipitate was washed with 95% ethyl alcohol, solvent exchanged with absolute ethanol and petroleum ether (30-60°C.), and dried in vacuo over calcium chloride and paraffin.

At this point, the hemicelluloses were still slightly colored. A precipitate formed upon addition of 72% sulfuric acid to a portion of the hemicelluloses, indicating the presence of lignin. Therefore, the hemicelluloses were dissolved in 2 liters of distilled water and sodium chlorite (40 g. over a 1-hr. period, pH 5, 35-45°C.) was again added. The reaction mixture was left at room temperature overnight. A small amount of undissolved material was removed by centrifugation. The hemicelluloses were precipitated, filtered, and dried as before.

ACETYLATION OF 4-O-METHYLGLUCURONARABINOXYLAN

A few grams of the hemicellulose were saved for future reference. The remainder was fully acetylated according to Carson and Maclay (22) as follows: Formamide (200 ml.) was added to 12-g. portions of the hemicellulose and shaken intermittently for 2 hours. Pyridine (400 ml.) was added, followed by the addition of acetic anhydride (300 ml.) over a 3-hour period with intermittent shaking. After remaining overnight at room temperature, the reaction was terminated by pouring the reaction mixture into 2 liters of ice and water. The precipitated gel was filtered, washed with 1 liter of cold 2% hydrochloric acid followed by 1 liter of cold water. This gel was very difficult to filter and attempts to solvent exchange the gel on a sintered glass filter were not too successful. The problem seemed to be stability of water retained in the gel. This problem was eliminated once the gel was broken with a solvent such as chloroform. Chloroform (approximately 200 ml.) was added with additional water as needed. The mixture was divided into several portions and evaporated on a rotary, vacuum evaporator until the acetate formed fairly firm clumps in the water suspension. The clumps were filtered and the particle size reduced in a Waring Blendor (one minute, in 95% ethyl alcohol). The acetate was then filtered, washed with 95% ethyl alcohol, solvent exchanged with absolute ethyl alcohol and petroleum ether (30-60°C.), and dried in vacuo over calcium chloride and paraffin.

MOLECULAR CHARACTERIZATION OF REDUCED AND UNREDUCED POLYMERS

The number average molecular weights, \bar{M}_n , of the reduced and unreduced polymers were determined by osmotic pressure measurements in an osmometer of the Zimm-Meyerson type. The membrane employed, Polypore Solvent Resistant Membrane Filter type 27G, is the densest membrane available. With this "superdense"

membrane, the rate of solvent permeation was very low and the attainment of equilibrium was quite slow. The time to equilibrium needed to be lowered to limit any possible polymer degradation. Thus, preliminary osmotic measurements were made for the GAX acetate using a less dense membrane (Polypore Solvent Resistant Membrane type 27F). These preliminary measurements were used to estimate the equilibrium points to be expected with the denser membrane. This permitted adjustment of the osmometer to nearly equilibrium conditions and lowered the time required to attain equilibrium.

The osmometer, with membrane in place, was rinsed carefully with TFE, filled, and allowed to condition overnight in the 30°C. bath. Fresh TFE was added and the osmometer was sealed and placed in a water bath ($30 \pm 0.02^\circ\text{C}.$). The difference in height (\underline{H}) of liquids in the reference and measuring capillaries was determined with a cathetometer after equilibrium was attained. This measurement, the "membrane constant" usually less than 1 mm., was subtracted from subsequent \underline{H} values observed with polymer solutions.

All measurements for both polymers were made with one membrane. Solutions of the two polymers were alternated in the osmometer with gradually increasing concentration. The membrane was conditioned overnight with each new solution. Fresh solution was then added for the actual measurement.

Calculation of molecular weight from osmotic pressure data depends on the fact that the following equation is rigorously correct:

$$M_n = RT/(\pi/c)_0 \underline{d}_1 g \quad (9)$$

where \underline{d}_1 is the density of the solvent, g is the acceleration due to gravity, \underline{R} is the gas constant, \underline{T} is the absolute temperature, π is the osmotic pressure

in g./sq. cm., \underline{c} is the concentration in g./cc., and the subscript indicates the value of π / \underline{c} must be taken at zero concentration. Determination of density can be avoided if the solution is made up by weight by using the concentration, \underline{w} , in g./kg. of solution and the osmotic height, \underline{H} , in centimeters, and Equation (9) for 30°C. becomes

$$M_n = 25,705 / (\underline{H}/\underline{w})_0 \quad (10)$$

The value, $(\underline{H}/\underline{w})_0$, is taken at zero concentration from a plot of $\underline{H}/\underline{w}$ as a function of \underline{w} .

With the Zimm-Meyerson osmometer, the number average molecular weights of the GAX and GAXR acetates were 17,700 and 18,000, respectively. This corresponds to molecular weights of 11,200 and 11,500 for the deacetylated GAX and GAXR polymers, respectively. These values are lower than those determined with the high-speed osmometer and this may indicate polymer degradation when the longer determination times were required for the Zimm-Meyerson type osmometer.

CHROMATOGRAPHIC TECHNIQUES

The hydrolysis of the pulp samples with sulfuric acid was identical to that outlined in the Saeman technique (33). Similarly, elution of the individual sugars from the chromatograms and colorimetric analysis using the Somogyi and Nelson reagents were identical to the above procedure. The modification concerned the analytical handling of the hydrolyzate.

The hydrolyzate was neutralized with barium carbonate and a known quantity of rhamnose was added from a stock solution of rhamnose (prepared in 0.2% benzoic acid and stored in a refrigerator). After centrifugation, the supernatant liquid

was concentrated to approximately 2 ml. in a conventional vacuum evaporator. The concentrated hydrolyzate was placed on the chromatogram with an ultramicroburet.

The Analytical Group's calibration curve was used to convert absorbance values to sugar quantities. A separate calibration curve was determined to convert absorbance values to rhamnose values. Quantity of polymer retained in the pulp sample may be calculated from the known amount of rhamnose added, the ratio of xylose to rhamnose values, xylose pulp blank, sample weight, and the polymer recovery factor. The calculation follows:

$$\text{Retention, mg./g.} = \frac{\frac{\text{Xylose value} \times \text{rhamnose added}}{\text{Rhamnose value} \times \text{sample weight}} - \text{Pulp blank}}{\text{Polymer recovery factor}}$$

The above techniques could not be successfully used to measure the low retentions achieved in some of the initially selected sorption conditions. It was evident that with low levels of retention a larger sample size would have to be used, but a total hydrolysis with sulfuric acid seemed undesirable due to the difficulty of analytically separating such a small amount of xylose from a very large amount of glucose. The sulfurous acid hydrolysis used by Leech (50) to measure the retention of a galactomannan appeared to be a particularly desirable technique for this case. This technique consists of partial hydrolysis of a 1-2 g. pulp sample with 3-5% sulfurous acid in a boiling xylene bath (135°C.) for 60-90 minutes. A known quantity of rhamnose is added as an internal standard after neutralization of the hydrolyzate to limit subsequent analytical handling. Separation and analysis of the individual sugars are accomplished as in the Saeman technique. A polymer recovery factor is calculated from the amount of xylose recovered after hydrolysis of a known quantity of polymer. The amount of xylose recoverable from the pulp prior to sorption is also determined.

Leech (50) did not find any galactose in the sulfuric acid hydrolyzate of the pulp residue after sulfurous acid hydrolysis. However, the sulfuric acid hydrolyzates of all the sulfurous acid hydrolyses in this study contained considerable quantities of xylose. The fact that the polymer was not completely hydrolyzed could be anticipated since the resistance of aldobiouronic acid to hydrolysis is well known. The disturbing fact was that polymer retentions measured by this technique at higher levels did not compare well with those measured by total hydrolysis with sulfuric acid. The polymer retentions measured with 3.5% sulfurous acid and a 90-minute reaction time were about 25% lower than those measured with sulfuric acid hydrolysis. Polymer retentions measured with 5% sulfurous acid and a 120-minute reaction time were about 25% greater than those measured with sulfuric acid hydrolysis.

The results obtained with sulfurous acid hydrolyses were of questionable value as an analytical measure of polymer retention. This difficulty was probably due, at least in part, to the irregular resistance of the uronic acid-xylose units to partial hydrolysis. Xylose is very susceptible to destruction by the conditions of hydrolysis and the rate of destruction is probably dependent upon the concentration of xylose in the reaction mixture. This concentration could be quite different when the hydrolyses of a sorbed and nonsorbed xylan are compared.